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STEP
Strategies for Today's
Environmental Partnership

Proceedings of the 1995 API and GRI Naturally Occurring Radioactive Material (NORM) Conference

Exploration and Production Department
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SESSION 1

MEASUREMENT AND SURVEY

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DETERMINATION OF NATURALLY OCCURRING RADIONUCLIDES IN SAMPLES FROM THE GAS AND OIL INDUSTRY.

Validation of Analytical Methods through an Interlaboratory Test Programme

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SUMMARY

The build-up of Naturally Occurring Radionuclides (NOR's), leading to the production of various types of Naturally Occurring Radioactive Material (NORM), is often encountered during gas and oil production c.q. treatment. This gives rise to increased health hazards to personnel and to an environmental waste management problem. Both the NOR's considered to be relevant for E&P samples and their analytical results in terms of activity concentration were found to be strongly dependent on the analytical contractor laboratory selected. This is caused by the lack of standardized procedures for the analysis of E&P NORM. In anticipation to future, more stringent NORM legislation on disposal and associated quantitative risk assessment projects, which may become endorsed by national authorities, the gas and oil industry is helped by quality assured, standardised NORM analysis procedures. Therefore, the identification of relevant NOR's and the validation of their analysis in various types of E&P NORM samples has been investigated at Shell Research Amsterdam by carrying out a literature study and an (dutch) interlaboratory test programme, respectively. The certification of the analytical results has been performed by a foreign (*i.c.* non-Dutch) institute. Only after the implementation of corrective actions as agreed by the participants, standardised analytical methods for E&P NORM samples could be defined. The standardised methods arrived at are described in general terms in this paper.

INTRODUCTION

NORM (Naturally Occurring Radioactive Materials) is a acronym generally used for substances in which Naturally Occurring Radionuclides (NOR's) show up in concentrations above about 0.1 Becquerel per gramme (Bq/g). In the gas and oil industry, the term NORM is commonly used to describe the products and by-products in which the radioactive progeny of the two long-lived parent radionuclides, ^{232}Th and ^{238}U either show up or become enriched due to production or treating processes. During oil and gas production process this progeny may, to some extent, be brought to the surface together with natural gas, with well-fluids like natural gas liquids, crude oil and water, and with solid particles.

As such, NORM will constitute a radiological hazard, *i.c.* delivering a so-called TENR (Technologically Enhanced Natural Radiation) dose to human beings. Two path ways for exposure can be distinguished:

- enhanced *external* radiation fields near and in production and treatment facilities c.q. equipment may deliver a TENR dose to (contractor) *personnel,* and
- *internal* contamination of (contractor) *personnel* during maintenance and repair practices (inhalation or ingestion of NORM) and of the *public at large* through uncontrolled disposal of NORM or NOR contaminated equipment into the environment (ingestion of NOR's via human food chain).

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Any TENR dose delivered to (contractor) personnel can be minimised by bringing in place Standard Operational Procedures (SOP's)[1], whereas any TENR dose delivered to the public at large has to be controlled by competent national authorities regulating NORM disposal practices. Presently, there is an increasing international environmental concern on the occurrence and build-up of NORM in the Non-Nuclear Industries (NNI). In the Malaysian federation, in various gas/oil producing US states as well as in the European Union (EU), stringent guidelines to control NORM in oil and gas production and in the processing/treating facilities are implemented[2,3], or are being drafted[3,4] and will be implemented into national legislation in the forthcoming years. Besides, a group of international bodies[a] has issued 'basic radiation safety standards', which in the absence of national radioactive substance legislation may be utilised as NORM guidance.

This type of legislation either addresses NNI NORM specifically, or includes NNI NORM. This is achieved by defining notification, intervention and/or clearance activity concentration levels of the individual NOR's present. Besides, also schemes for compulsory, regular external and internal surveys of E&P facilities and equipment, may be an integral part of this type of legislation. Though activity concentrations forms the heart of the legislation, references to standardized (analytical) methods on sampling, sample pre-treatment and NOR analysis are neither included, nor recommended. To the best of our knowledge no such standardized methods have been issued yet for E&P NORM samples, neither have analytical contractor laboratories been identified who are working according to (quality assurance) certified procedures.

The need for standardization has been clearly experienced in practice. On several occasions it has been observed that results from E&P NORM analysis on pre-treated, homogenised samples from the gas/oil industry by Dutch authorized institutes with experience and expertise in NORM analysis, showed large mutual scatter for various analyses results. In view of the great (economic) impact the use of unreliable working procedures might have for E&P industry; the lack of certified procedures for E&P NORM sampling and analysis; the strongly growing awareness of the need for standardisation in environmental screening matters, and the potential liabilities, it is needless to state that both sampling and analysis methods, which both are reliable, standardized and acceptable to the competent authorities, are a critical need.

In practice, the availability of adequate and proper NORM sampling an analysis methods would allow: *1)* to enable accurate determination of the strict radiological levels on-site, *2)* to qualify and to process production facility parts as well as secondary streams and waste, *3)* to enable reporting to authorities of NORM activity concentrations involved, and *4)* to carry out reliable quantitative risk assessments. The availability of these methods will also strengthen the negotiating position of the E&P industry in discussing NORM levels with national authorities.

The importance of sampling, being the first step in the analysis sequence, has not been neglected nor has it been underestimated. In fact, poor sampling degrade all values of subsequent activities as it wastes time and effort thereby requiring repeat samples to confirm uncertain results. Despite its important contribution to the uncertainty of the NORM results, the standardization of NOR analysis of samples stemming from the E&P industry (*i.e.* gas, hydrocarbon condensate, water, scale and sludge) has been the subject of a research project at Shell Research Amsterdam. Because of the highly specific character of these sample types with respect to the sample composition and the NOR's present therein, and because of the impact of the NOR activity concentration on the measures following from national legislation, standardization of NORM analysis techniques was considered to be essential. An interlaboratory test programme on NORM analysis using pre-treated, homogenised actual samples from the gas and oil production and treatment facilities has been set up, in order to achieve this goal. The way in which the interlaboratory test programme has been conducted, has extensively been described[5]. Next to a short summary, the results obtained will in particular be described in this paper.

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[a] FAO [Food and Agriculture Organisation], International Atomic Energy Agency [IAEA], ILO [International Labour Organisation], NEA/OECD [Nuclear Energy Agency of the Organisation for Economic Cooperation and Development], PAHO [Pan American Health Organisation] and WHO [World Health Organisation].

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E&P NORM CHARACTERISTICS

Naturally Occurring Radionuclides (NOR's) which are omnipresent on the planet *earth*, can be subdivided into cosmogenic (*e.g.* ^{7}Be, ^{14}C) and primordial (*e.g.* ^{40}K, ^{87}Rb, ^{138}La, ^{190}Pt, ^{232}Th, ^{238}U) radionuclides. While cosmogenic radionuclides are continuously formed in the outer atmosphere by cosmic irradiation, primordial (or terrestrial) radionuclides have been present ever since the *earth* (lifetime 5.5×10^{9} y) has been formed.

Uranium (U) and Thorium (Th) are spread throughout *earth*'s crust, at an average concentration of 4.2 and 12.5 ppm(w/w)[6]. The naturally occurring U- and Th-isotopes being ^{235}U (natural abundance: 0.72%), ^{238}U (99.28%) and ^{232}Th ($\approx$ 100%), are radioactive. Due to its low isotopic abundance, ^{235}U is rarely encountered in practice and therefore this series will not be further be discussed here. Consequently, 'radioactivity' is also wide-spread in the environment, on average 0.05 Bq[^{238}U]/g and 0.05 Bq[^{232}Th]/g.

The primordial radionuclides ^{232}Th and ^{238}U, are special radionuclides, as they each are heading a series of successive nuclear decays (Figs. 1 and 2). Both these NOR's decay through essentially the same elements, all of which are radioactive. As such, these radioactive daughters can be present in gas and oil bearing formations as NOR's, where next to gas and oil also formation water is present in varying amounts.

If a geological formation containing ^{232}Th and ^{238}U has not been disturbed ('closed system') for more than 10^{6} years, all members of both decay series will have the same activity concentration (Bq/g) and the series is said to be in *secular equilibrium*. However, as the chemical concentration (mole/g) is proportional to the half-life time ($t_{\frac{1}{2}}$) of a radionuclide, their number of atoms varies considerably. When a formation is not 'closed' to radionuclide migration, *e.g.* ^{226}Ra becomes mobilised and is 'deposited' somewhere outside the formation, the secular equilibrium will be disturbed. At the site of deposition the only way the ^{226}Ra concentration can stabilise or increase is by influx of (geo)chemical/physical transport phenomena. No ingrowth of ^{226}Ra via radioactive decay of its ancestors will occur as all radionuclides above ^{226}Ra (*cf.* Fig. 2) will stay close ^{238}U. In this way at the site of deposition ^{226}Ra is *unsupported*, *i.c.* ingrowth is not supported by radioactive decay.

The (geo)chemical/physical properties of all radium isotopes, *i.c.* ^{226}Ra, ^{228}Ra and ^{224}Ra, are identical. Differences between these isotopes are caused by their radiation decay characteristics and hence by the associated potential radiation hazards. A NOR should 'live' long enough to develop the (geo)chemical properties of the element. In gas and oil production two typical time scales are important, a *geological* (say, far longer than 1,000 years) and a *production time scale* (order of magnitude: days to decades). Therefore, for processes taking place on a time scale of one day, only isotopes of thorium, radium, lead, uranium, radon and polonium may become unsupported. From considerations with respect to the formation of hydrocarbons from source rock under reducing conditions[7], from considerations with respect to geochemical transport phenomena[8] and from an extensive literature survey[9], only a limited number of NOR's actually may appear unsupported in E&P (by-)product streams.

The survey showed that both ^{238}U (and its immediate daughters: ^{234}Th, ^{234m}Pa, ^{234}U and ^{230}Th) and ^{232}Th were only present in minute quantities ($\ll$ 0.05 Bq/g), which is in agreement with transport phenomena under reservoir conditions. Consequently in E&P samples the NOR's mentioned do not constitute a radiological hazard.

Furthermore, it was observed that radium isotopes actually mark a clear separation line for the encounter of NORM in gas/oil production, treating or processing facilities. The most likely cause for this separation is a distinct difference in geochemical properties (mobility under reservoir conditions) in combination with the effective[b] half-life of ^{238}U and ^{232}Th on one hand, and that of ^{226}Ra and ^{228}Ra and their progeny

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[b] The effective half-life of a radionuclide under reservoir conditions is defined as a linear combination of its physical half-life ($t_{\frac{1}{2}}$) and its 'mean residence time' in a phase during production from the reservoir or even during maturation, migration or accumulation processes in the subsurface.

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on the other hand. As in the ^{232}Th series in between ^{228}Ra and ^{224}Ra, rather long-lived (with respect to a production time scale) and (geo)chemically immobile ^{228}Th is encountered, ^{228}Ra and ^{224}Ra are normally not in secular equilibrium, and hence for radiological assessment studies, production water and production water associated deposits have to be analyzed both for ^{228}Ra and ^{224}Ra.

For relatively dry natural gas wells, ^{222}Rn forms a second distinct separation line for the potential encounter of NORM. Most likely the ^{222}Rn stems from (reservoir) rock near the perforation.Very often it is observed that with increasing depletion of gas reservoir due to production also increasing ^{222}Rn concentrations are found.

From the survey it was also observed that also ^{210}Pb may mark an independent separation line in the ^{238}U decay series, as this radionuclide can be encountered unsupported. When carried with the water phase, this is likely caused by its specific (geo)chemical properties, but also indications exists that ^{210}Pb is transported through the gas phase[10].

Only one case of unsupported (highly radiotoxic) 210Po in hydrocarbon condensate has been reported, notwithstanding the fact that one should be aware that this radionuclide may be encountered.

From the geochemical considerations and observations done during the survey, E&P samples should be analyzed for NOR's according the scheme presented in table 1. These types of analysis were requested during the interlaboratory test.

Table 1: NOR's encountered in E&P samples

E&P (by-)product stream	^{238}U progeny	^{232}Th progeny
Natural Gas	^{222}Rn	none
- Natural Gas Liquids	^{222}Rn, ^{210}Pb, ^{210}Po	none
Crude Oil	none	none
Production water	^{226}Ra, ^{210}Pb	^{228}Ra, ^{224}Ra
- hard scale	^{226}Ra	^{228}Ra, ^{224}Ra
- medium hard to soft scale	^{226}Ra, ^{210}Pb	^{228}Ra, ^{224}Ra
- scrapings	^{226}Ra, ^{210}Pb	^{228}Ra, ^{224}Ra
- sludge	^{226}Ra, ^{210}Pb	^{228}Ra, ^{224}Ra

INTERLABORATORY TEST PROGRAMME

The interlaboratory test programme, with participation of eleven Dutch institutes that are known to have expertise in NORM analysis, has been described in detail elsewhere[5]. The test programme consisting of four stages and was conducted over a period of three years. The actual oil and gas production samples varied from relatively simple single phase (*e.g.* methane gas, hydrocarbon condensate, production water and scale) to complex multi-phase samples (*e.g.* various sludge samples). After a pretreatment step to achieve homogeneity and a check via repeatability measurements, the samples were despatched to the participants. After 3 months results were collected and subjected to statistical evaluation and feedback was given to the institutes via a review meeting (*i.e.* discussion of the results, exchanging analytical expertise, agreeing on measures to be taken and on samples for the next stage).

Prior to the despatch, the homogeneity of each sample was determined at Shell Research Amsterdam by repeatability measurements using γ-spectrometry, except for *(i)* the condensate, where radiochemical ^{210}Po analysis (*vide infra*) was applied, and *(ii)* the methane gas where the ^{222}Rn analysis via the α-scintillation method (*vide infra*) was used. With reference to the estimated counting statistics error, the repeatability was less than 5% at 95% confidence level (2σ), while, the more laborious radiochemical technique (^{210}Po) did show a somewhat larger repeatability.

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Except for the first stage of the test programme, in which results were compared to those obtained by Shell Research Amsterdam, the activity concentrations of γ-emitting NOR's in the samples were certified by the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig, Germany. However, PTB could not certify the α-activity concentration of ^{222}Rn in methane gas and that of ^{210}Po in the other samples. Therefore, to enable mutual comparison of the ^{210}Po results, an aliquot of an aqueous ^{210}Po standard has been analyzed by the institutes in stage four of the test programme.

ANALYSIS TECHNIQUES

The full radiometric analysis of E&P NORM samples generally requires at least three techniques for a complete determination of the activity concentrations of the various NOR's:

Lucas cell α-scintillation method for the determination of ^{222}Rn in natural gas

The inner surface of a cylindrical Lucas cell (± 250 mL) is coated with a high-efficiency α-scintillator material (e.g. zinc sulphide). Natural gas is introduced in the cell, which will be light-tight connected to a photomultiplier tube. After about two hours ^{222}Rn will be in secular equilibrium with its short-lived progeny, particularly its α-emitting daughters ^{218}Po and ^{214}Po (*cf.* Fig. 2). The ^{222}Rn concentration is computed from the number of detected scintillations (efficiency calibration required) due to α-decay. This measurement technique is fast, simple and easy to operate. Analytical results will be available at the same day.

γ-spectrometry for the determination of ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{224}Ra in various types of E&P samples

A γ-spectrometer consists of a high efficiency, high energy resolution ($\Delta E/E < 0.2\%$), (non-)doted germanium detector, which is placed in a low background radiation area obtained by shielding with (old) lead bricks. In general E&P samples can be measured as received, but in some cases sample pre-treatment (*e.g.* for sludge the sample is separated into a liquid and solids part) is required. The sample is placed in a standard size, air-tight container on top of the detector and the current pulses in the biased semi-conducting germanium detector are registered. Spectrometer efficiency calibrations (including corrections for true coincidence) are performed using NORM reference materials. Both the quick analysis (results after about two days) and the accurate analysis (about one month) require expert knowledge and can not be carried out by a layman.

- The ^{226}Ra concentration can be computed accurately from the registered γ-emission intensity of its indirect daughter isotopes ^{214}Bi and ^{214}Pb. Therefore, an air-tight sample container has to filled and stored in order to establish secular equilibrium between the isotopes, which is reached after about three to four weeks.

  However, because of the absence of ^{235}U (a.o. γ-emission line at 185 keV), a quick and somewhat less accurate analysis can be performed in about one day by direct measurement of the 186 keV ^{226}Ra γ-emission line.
- The low γ-energy 46.5 keV line of ^{210}Pb can be determined only if a sensitive germanium detector is available. E&P NORM samples often have a relatively low activity concentration and a high density. As a result, γ-attenuation in the sample will occur, which has to be taken into account during calibration of the γ-spectrometer system. A correction for self-absorption of ^{210}Pb and/or other γ-photons of low energy has been made (*e.g.* via γ-transmission measurement[11] or via computed efficiencies from effective solid angles[12]). Correction factors between 1.5 and 2.5 are not exceptional, particularly when high Z elements (*e.g.* Ba, Pb) are present.
- After establishing secular equilibrium (in about one day) with its immediate daughter ^{228}Ac, the ^{228}Ra concentration can be computed from a selection of the most intense ^{228}Ac γ-lines.
- After establishing secular equilibrium (in about two days) with its indirect daughters ^{212}Pb, ^{212}Bi and/or ^{208}Tl, the ^{224}Ra concentration is computed from a selection of their most intense γ-lines present (*cf.* Appendix).

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α-spectrometry for the determination of ^{210}Po in various kinds of E&P samples

An α-spectrometer is an evacuated (to enhance the mean free path of α-particles) chamber, in which a silver disc with the deposited α-emitter is placed opposite an α-energy discriminative detector. A fluid (*water* reduced by evaporation; *hydrocarbon condensate* acid extracted and subsequent reduction by evaporation) E&P sample is spiked with ^{208}Po, while a solid E&P samples is acid digested and the obtained solution is spiked with ^{208}Po and reduced by evaporation. Both ^{210}Po and ^{208}Po (internal calibration of deposition efficiency) are deposited onto the silver disc. The method is very labour intensive and requires expert knowledge. It has a low detection limit, while results may be available after about one day.

Details on the methods applied, such as detection limits, accuracy, preparation and measuring time, are listed in Table 2:

Table 2: Characteristics of the NORM analysis methods applied.

NORM Analysis Method	Type of sample material	Detection limits for each NOR	Accuracy (2σ at 95% conf. level)	Preparation time (hours)	Measuring time (hours)
γ-spectrometry ^{226}Ra, ^{210}Pb, ^{228}Ra, ^{224}Ra	Solid Liquid	0.02 Bq/g 0.01 Bq/g	10% 10%	0.25 to 2.0 0.25 to 0.5	15 15
α-spectrometry ^{210}Po	Aqueous solutions Solid Condensates	4×10^{-6} Bq/g 4×10^{-3} Bq/g 0.5×10^{-3} Bq/g	10% 10% 10%	3 5 3	15 15 15
α-scintill. cell ^{222}Rn	Natural gas	0.01 Bq/L (STP)	10%	0.25 to 0.3	3 to 5

RESULTS AND CONCLUSIONS OF THE TEST PROGRAMME

During the interlaboratory test programme, the need for standardization of E&P NORM analyses on samples from the gas and oil industry, which are highly specific (in terms of NOR's present, required (pre)treatment techniques, sample composition, *etc.*), was clearly demonstrated. After each stage, a steady improvement in the reproducibility and accuracy of the analytical results was shown which may partly be attributed to the open character of exchanging analytical expertise during the review in meetings. As such, the participation in the test programme on NORM analysis proved to be beneficial to all parties involved.

With few exceptions only, the NORM analyses methods used at the Dutch institutes were proven to be reliable and accurate. Next to locally standardized methods at several institutes, those used by Shell Research Amsterdam were proven to be reliable and accurate throughout the test, and were found to be a sound basis for broader standardization of E&P NORM analyses.

As described above only three distinct analytical methods are required to fully characterize E&P NORM samples, thereby yielding complete accurate and reliable results (Table 2).

a) α-scintillation counting using a Lucas cell for the determination of ^{222}Rn in natural gas.

b) γ-spectrometry for determination of ^{226}Ra, ^{210}Pb, ^{228}Ra and ^{224}Ra ('γ-emitting NOR's') in the solid and liquid E&P NORM samples. Compared to radiochemical methods, this technique is fast, precise, accurate and yields a multi-nuclide analysis.

c) acid digestion of the sample spiked with ^{208}Po standard, followed by spontaneous deposition of polonium on silver, followed by α-spectrometry to measure the ^{210}Po concentration in the solid and liquid NORM samples.

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The critical parameters in the application of these methods were:

ad a) the use of methane gas for counting cell efficiency calibration, by purging methane gas through a standard ^{226}Ra solution in secular equilibrium with ^{222}Rn. It is essential that the density of the purging gas should correspond to that of the sample to be measured, as the counting efficiency of the cell increases with the decreasing gas density inside the chamber[13]. In case nitrogen is used as purging gas, the ^{222}Rn counting cell efficiency for natural gas will be too low by some 7%. Besides, ^{226}Ra calibration source available from manufacturers, from which ^{222}Rn is purged by air, is only suited for this purpose, if appropriate corrections for purge gas density are made.

ad b) an accurate correction for self-absorption, in view of the low energy γ-emission of ^{210}Pb at 46.5 keV and the heavy matrix of the majority of the samples analyzed. A simple and adequate correction technique for self-absorption is based on γ-transmission measurements[11]. This technique only requires the attenuated and unattenuated beam intensity of a ^{210}Pb point source to correct for self-absorption due the sample matrix at the 46.5 keV γ-line.

a uniform NOR's γ-yield data set, based on recent insight/investigations in order to obtain reproducible/reliable results for the complex sludge samples. An inventory of the NOR 'γ-yields' applied by the institutes to calculate activity concentration, showed that amongst them values varying up to 30% were used. These γ-yields are often included with the commercially available data-acquisition and data-analysis software packages, whereas more recent literature values are also used. To exclude errors in results due to variation in 'γ-yields', it was agreed to use a uniform set of recently revised 'γ-yield' data[14,15,16] for all γ-spectrometry results reported (*cf.* Appendix), after which a clear improvement in accuracy of the results has been observed.

ad c) a well-calibrated ^{208}Po spike solution, for the ^{210}Po measurement. The accuracy of the ^{210}Po activity concentration analysis has been checked using a commercially available, aqueous ^{210}Po standard. Trends observed in the analytical results produced by the participants disappeared when corrected with the analytical results obtained for an aliquot of a commercially available ^{210}Po standard. Therefore, it could be concluded that the accuracy of the results is affected by that of the ^{208}Po standard rather than by sample digestion procedure and the α-spectrometry techniques.

The observed improvement in accuracy during the four stages of the test programme were shown to be independent of the applied instrumentation and data-analysis software packages. The improvement in the γ-spectrometric results averaged per stage, and normalized to PTB or Shell Research Amsterdam reference values is shown in Figure 3. With reference to a range set by the average PTB result ± 10%, a gradual improvement in the results may be observed in comparison with each preceding stage, which is noteworthy, especially for the complex sludge samples in Stage 3. For the ^{226}Ra results sludge 1 of Stage 4, it should be noted that a general trend has been observed, indicating that the PTB result might be inaccurate. For the complex sludge samples of the final Stage 4, all results reported are within ± 10% of those reported by PTB, except for two institutes (04 and 09).

Due to lack of standardized and (internationally) approved on-site NORM sampling techniques for products, by-products and waste materials from gas and oil production and treatment industries, this item was not included in this study. It may, however, still be a major cause of discrepancies in the results from NORM analysis, and therefore is currently the subject of future research.

CONCLUSIONS

The oil/gas industry should be well aware that through the build-up of unsupported NOR's, contamination of the decay products of ^{238}U and ^{232}Th may occur in its streams, (by)products and (part of) its installations;

- E&P samples do generally not include the 'parents' ^{238}U and ^{232}Th at levels constituting a radiological risk.
- Radium is the first 'daughter' element encountered, ^{226}Ra and ^{228}Ra respectively.
- E&P samples may contain unsupported NOR's, ^{226}Ra, ^{222}Rn, ^{210}Pb and ^{210}Po (^{238}U-series) and ^{228}Ra and ^{224}Ra (^{232}Th-series).

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Three distinct NOR's analysis techniques are required to perform a full radiometric analysis of E&P NORM samples:

- *for natural gas samples*: Lucas cell α-scintillation method (^{222}Rn).
- *for solid and fluid samples*: γ-spectrometry (^{226}Ra, ^{210}Pb, ^{228}Ra and ^{224}Ra) & α-spectrometry (^{210}Po).

From the interlaboratory test programme, the following items may introduce large errors in E&P NORM analysis results:

- Lucas cell α-scintillation method: the choice of the purge gas for the efficiency calibration of the cell.
- γ-spectrometry: the correction technique used for self-absorption correction in case of ^{210}Pb, and the selection of 'γ-yield' data for conversion to other NOR specific activity concentrations;
- α-spectrometry: the accuracy of the ^{208}Po 'spike' used for ^{210}Po analysis, and

In view of the importance of the findings to all institutes as a first step to standardisation, the results of the interlaboratory test programme on NORM analysis have been published in a joint multi-institute co-authorship[5]. As such, these NORM analysis methods will not be prescribed in a strict manner to the operating companies, but the various attention points therein which may lead to erroneous results have clearly been indicated.

Finally, also the standardisation of methods for E&P NORM sampling is, as far as possible, is a critical need. A generic standardisation for E&P sampling is currently the subject of a currently ongoing research program at Shell Research Amsterdam.

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Appendix NOR γ-YIELD DATA USED, STARTING WITH STAGE 3

Series	Sub-series	in secular equilibrium with	γ-emitting isotope	γ-photon energy (keV)	γ-photon yield (%)
^{232}Th	^{228}Ra	^{228}Ac	^{228}Ac	338.4	11.50
				911.1	25.30
				969.1	15.40
	^{228}Th (^{224}Ra)	^{224}Ra, ^{220}Rn, ^{216}Po, ^{212}Pb, ^{212}Bi, ^{212}Po/^{208}Tl	^{212}Pb	238.6	43.10
				300.0	3.34
			^{212}Bi	727.3	6.93
			^{208}Tl	583.1	29.40
				860.6	4.32
				2614.5	34.20
^{238}U	^{238}U	^{234}Th, ^{234m}Pa, ^{234}U, ^{230}Th	^{234}Th	63.3	3.81
				92.8	5.57
			^{234m}Pa	1001.0	0.79
			^{230}Th	67.7	0.37
	^{226}Ra	^{222}Rn, ^{218}Po, ^{214}Pb, ^{214}Bi, ^{214}Po	^{226}Ra	186.1	3.51
			^{214}Pb	258.8	0.55
				295.2	19.30
				351.9	37.60
				480.4	0.32
			^{214}Bi	389.1	0.42
				609.3	46.09
				665.5	1.56
				719.9	0.38
				768.4	4.94
				806.2	1.22
				934.1	3.03
				1120.3	15.10
				1155.2	1.63
				1238.1	5.79
				1281.0	1.43
				1377.8	4.00
				1385.3	0.78
				1401.5	1.27
				1408.0	2.15
				1509.2	2.11
				1661.3	1.15
				1729.6	2.92
				1764.5	15.40
				1847.5	2.12
				2118.5	1.21
				2204.0	4.99
	^{210}Pb	^{210}Bi (^{210}Po)	^{210}Pb	46.5	4.00

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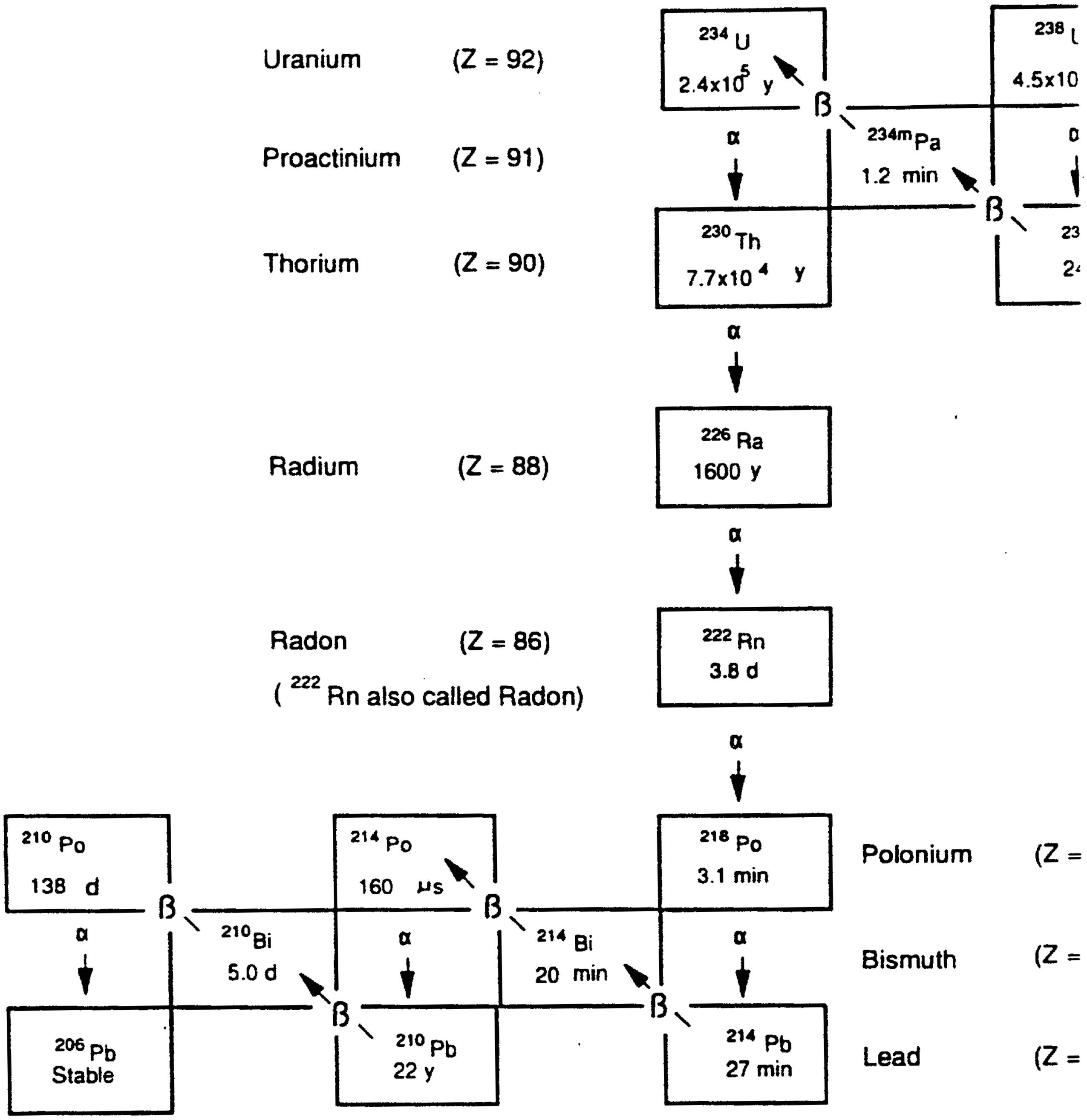

Figure 1

Principal decay scheme of ^{238}U. The chemical symbol (or atomic number Z) reflects the chemical properties, the 'superscript' isotopic number (or atomic mass) reflects the radiation properties. α-decay lowers the atomic number with 2 and atomic mass with 4. β-decay increases the atomic number with 1, while the atomic mass remains the same.

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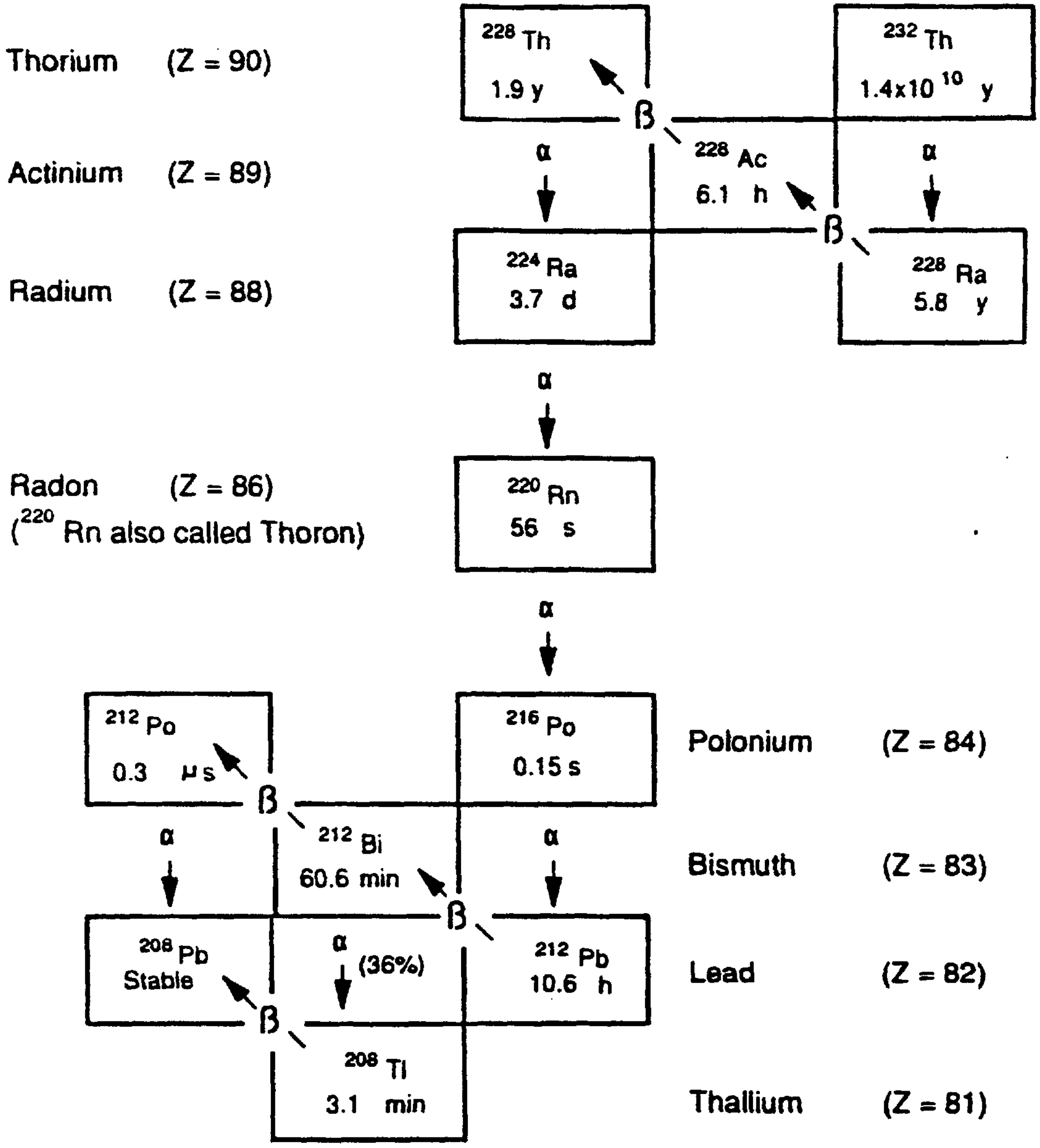

Figure 2
Principal decay scheme of ^{232}Th. The chemical symbol (or atomic number Z) reflects the chemical properties, the 'superscript' isotopic number (or atomic mass) reflects the radiation properties.
α-decay lowers the atomic number with 2 and atomic mass with 4.
β-decay increases the atomic number with 1, while the atomic mass remains the same.

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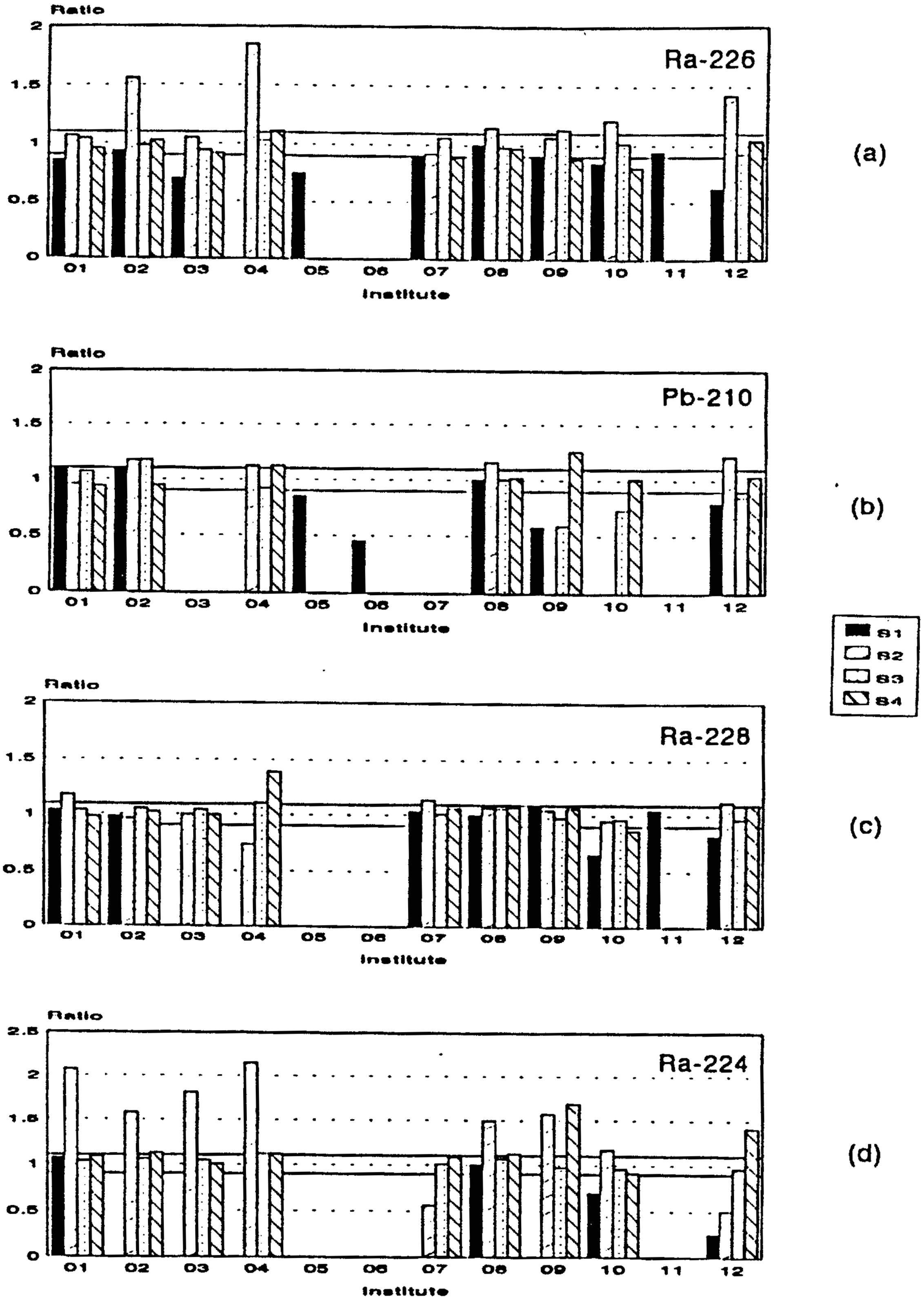

Figure 3
Accuracy improvement trends of averaged NOR γ-spectrometric results for each stage (S1 to S4) of the interlaboratory test programme. Results as well as a 10% error range are shown, relative to the results of the reference institute (*i.e.* PTB).

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DETECTING NORM CONTAMINATED TUBING DURING PULLING OPERATIONS

T. M. Williams, Texaco, Inc., EPTD

ABSTRACT

A system has been developed and field tested that can detect NORM contaminated tubing as it is pulled from a well. Early, automatic identification of contaminated tubing can reduce the manpower required to manually survey all tubing for contamination. Early detection will also allow field personnel to separate the contaminated tubing and handle it as needed to prevent the spread of contamination.

The system is composed of a sodium iodide detector and an alarming rate meter that can be mounted remotely. The alarm level is adjustable so it can be set to the desired level for different tube sizes, installation geometries, and background levels.

INTRODUCTION

Oil well tubing contaminated with NORM (Naturally Occurring Radioactive Material) is found in many producing fields. To reduce the manpower requirements needed to identify contaminated tubing, we have developed and tested a system to identify contaminated tubing as it is pulled from a well.

To reduce the cost of development and reduce the final cost to users, we tested components of several commercial instruments. We laboratory tested several systems and selected two of them for a field test. One of the systems selected for a field test was mounted in an explosion proof box such as may be required in hazardous locations.

Field tests have been held in west Texas and near offshore Louisiana. The field tested systems consisted of a 3×3 inch sodium iodide crystal detector and an alarming ratemeter. The systems were able to detect the contaminated tubing above 50 μR/hr.

Systems such as the ones tested can be packaged for use in oil fields and mounted on workover rigs with the alarm positioned near the rig operator. The systems could be combined with an automatic marking system that would mark any tube section that caused the system to alarm.

DISCUSSION

Several manufacturers have developed instruments to detect various types of radiation under many conditions. For the needs of this project, we decided a sodium iodide crystal detector was the best detector because of its high detection efficiency and relatively low cost. Among the items tested were a *Gate Frisker* and an *Alarming Ratemeter* coupled with three different sodium iodide (NaI) detectors.

The systems originally tested were not designed for use in hazardous locations or for use in bad weather. Based on successful field tests of two of those systems, a system designed for use in Class I, Division 1, Group D hazardous locations was tested offshore Louisiana.

The system field tested in Louisiana consisted of an enclosure that contained a shielded, 3×3 inch, sodium iodide crystal detector. This enclosure was connected to an alarming rate meter by a fifty foot long cable. All signals in the cable were "intrinsically safe" so the cable

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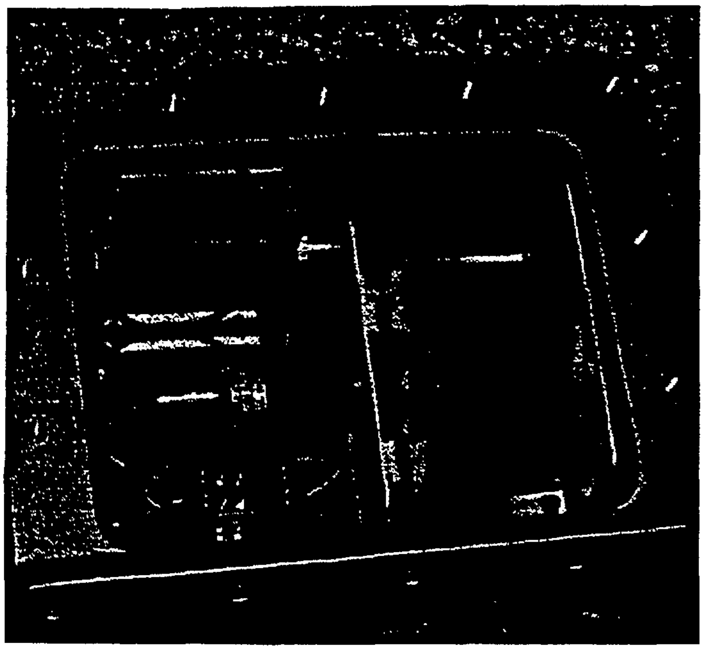

Figure 1 Detector in Explosion Proof Enclosure

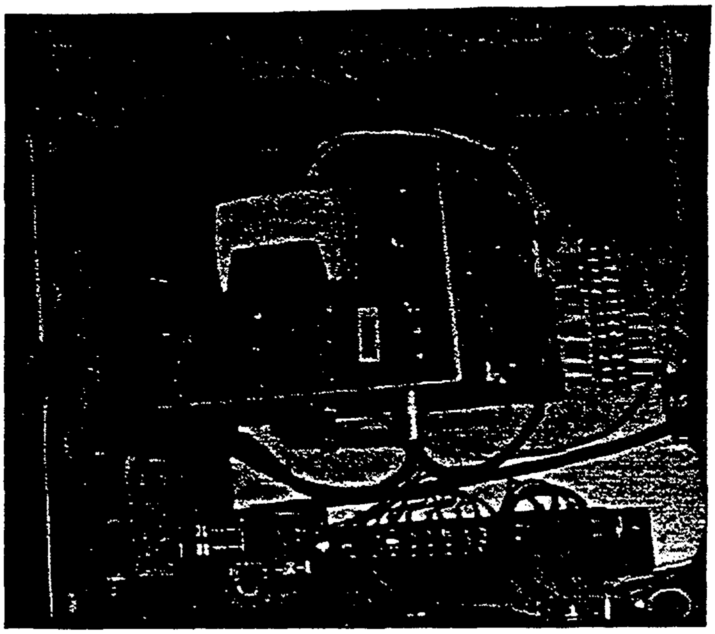

Figure 2 Ratemeter and Enclosure

could be run in hazardous locations. The alarming rate meter was placed in a weather tight enclosure that was not rated for hazardous locations. With minor changes, the entire system could be designed for operation in hazardous locations.

The rate meter counts the gamma rays detected by the detector and displays the count rate on an analog meter. A 4 position switch can be adjusted to change the full scale value. For the second field test, switches were mounted on the outside of the enclosure to allow the:

1. Alarm level to be displayed,
2. Alarm level to be adjusted,
3. Alarm to be reset, and
4. System to be turned on/off.

There systems tested were designed to operate on internal batteries or on standard 120 volt power. The batteries can power the system for over 24 hours.

Laboratory Tests

Laboratory tests were performed at Texaco EPTD's Bellaire, Texas facility using several different instruments to determine if it is feasible to use commercially available instruments to detect NORM contaminated tubing as it is pulled from a well. The tests indicated it is feasible, however some changes will be required to optimize them for oil field applications.

We tested several different sodium iodide crystal detectors and an alarming ratemeter. The alarming ratemeter used had a pulse output that was connected to a computer controlled multichannel scaler. Thus the count rate as a function of time could be recorded for later analysis.

For the tests, a small radium calibration source was placed inside a three inch, schedule 40, steel pipe. The source caused a maximum dose rate of 25 μR/hr at the surface of the pipe. A physically small and relatively weak source was picked as a "worst case." Distributed sources will cause a stronger detector response.

The detector of the instrument under test was placed a measured distance from the center line of the pipe. The pipe was lowered and then raised passed the detector under test. The counts in the detector were recorded. The distance from the detector to the pipe was changed and the test repeated.

Tests to simulate different pulling speeds were also performed. Pulling speed of 1000 to 5000 ft/hr were simulated in 1000 ft/hr increments.

Tests were performed using 2×2 inch and 3×3 inch sodium iodide detectors. One of the 3×3 inch detectors was shielded to reduce background count rate. The other detectors were unshielded. Tests were also performed using a one inch thick plate of aluminum to simulate the presence of an explosion proof housing. The aluminum plate reduced the counts in the detector, but the 3×3

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inch detectors were able to detect the presence of the radioactive source.

The source was kept in the pipe by a cap that was clamped onto the pipe. On some data runs, the 2 x 2 detector could not detect the radioactive source. The instances of non detection were probably caused by the pipe rotating into a position that placed the clamp hinge between the source and the detector. This additional thickness of steel would significantly reduce the detectable counts from the source. Based on these tests, it was determined that a 2 x 2 detector could not reliably detect low levels of NORM contamination under typical field conditions.

Figure 3 shows the results from a 3 x 3 inch detector for three different distances between the source and detector at 5000 ft/hr. The counts are in one second intervals. The data from the pass when the source is nearest the detector shows the most counts. With this detector at any of these three source to detector spacings, the system would alarm if the alarm level was set to 1-1/3 the average background count rate.

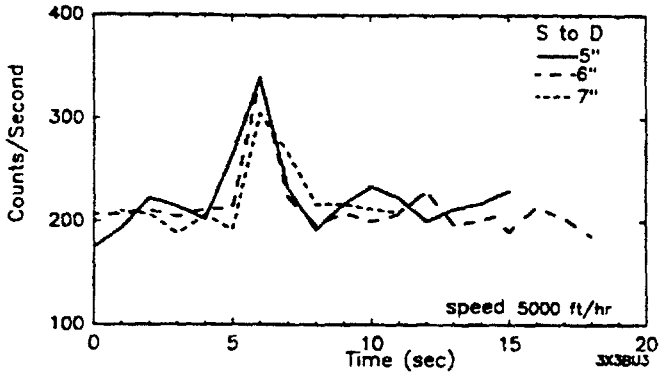

Figure 3 3 x 3 NaI Detector at 5000 ft/hr.

Different pulling speeds also effect the detector response. This effect can be seen in Figure 4. The slower speeds cause a higher response and a wider peak. This effect will probably not be as pronounced with a distributed source such as will be usually seen in the field because with contamination spread over several feet of tubing, the contaminated area would be detectable for several seconds.

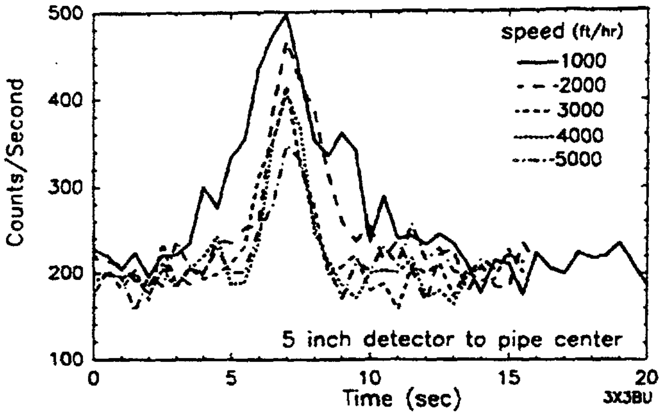

Figure 5 3 x 3 Inch Unshielded Detector at Various Pulling Speeds

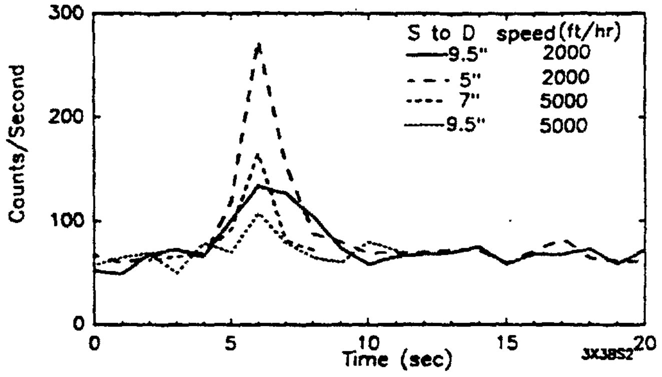

Figure 4 3 x 3 NaI Shielded detector results.

For the shielded detector, the response is similar. The average background count rate is only about 1/4 of the background count rate of the unshielded 3 x 3 inch detector and about 1/2 the unshielded 2 x 2 inch detector. The lower background makes it easier to detect low levels of NORM contamination. The results of some measurements with a shielded detector are shown in Figure 5. This plot shows different spacings and different pulling speeds. The closer the detector is to the source and the slower the pulling rate, the higher the response in the detector.

As a result of the laboratory tests, the 3 x 3 inch sodium iodide detector was selected as the detector to be used in the field test.

Field Tests

Two successful field tests of the NORM pipe detector have been performed. The first one was in west Texas and the second offshore Louisiana. For the west Texas test, contaminated 2-1/2 inch tubing was brought in from another well.

For the field test, a 16 inch long spool piece of 6 inch casing was installed between the BOP's and the pipe slips. Openings were cut in the sides of the spool pieces

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to improve detection efficiency. The enclosures containing the detectors were clamped onto the spool piece flange. An improved method of mounting in locations that do not require equipment to rated for hazardous atmospheres may be to weld a "mounting tube" onto the side of the spool piece or to mount it in the branch of a tee. The mounting tube should have an ID sufficient to accept the detector with some padding to reduce detector vibration. The end of the mounting tube should be made of 1/4 inch or thinner steel to keep source attenuation to a minimum.

For the first field test, one shielded, 3 × 3 inch, sodium iodide crystal detector was mounted in a NEMA 12 enclosure and connected to an alarming ratemeter. Output from the ratemeter was connected to a multichannel scaler data acquisition card in a portable computer. The detector was mounted about 5 inches from the center of the tubing.

A second shielded 3 × 3 inch sodium iodide crystal detector was mounted in an explosion proof box such as may be required in hazardous areas. The detector in this box was mounted about 7-1/2 inches from the center of the tubing.

The contaminated tubing had various levels of contamination along its length. One spot near the bottom of the tubing measured 200 μR/hr. Other sections of the pipe had less contamination. Figure 6 is a plot of some field test data. The first peak shows the detector counts as the contaminated tube was slowly pulled from the well.

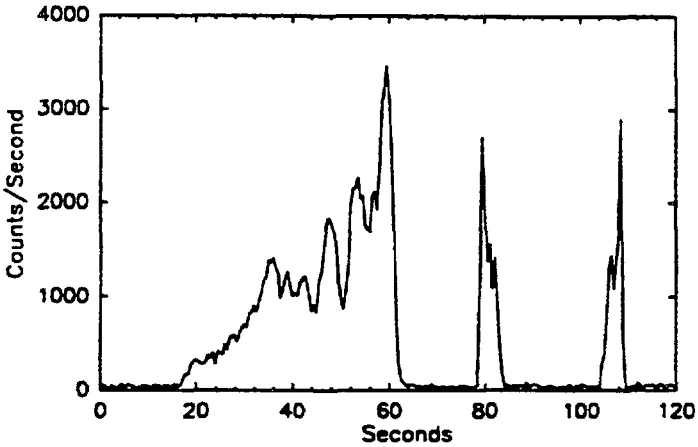

Figure 6 Field Test Detector Response

The slow pulling rate (≈ 4,000 ft/hr) allows a profile of the contamination to be easily viewed. The shape of the peak shows that the contamination about 5 feet from the top of the tube is about 1/3 what it is near the bottom. If we assume that 200 μR/hr causes 3000 counts/sec in the detector and the response is linear then a response of 750 counts/sec will be caused by a field of 50 μR/hr. That count rate is well above the background count rate of this detector. Thus, the alarm level could be adjusted to detect contamination levels ≤50 μR/hr with little chance of false alarm.

The second and third peaks show the tube being rapidly lowered into and then pulled from the well. These peaks have the expected shapes when compared to the first peak. The faster pulling rate (≈ 19,000 ft/hr) data indicates that even though the maximum count rate was reduced, the count rate is still significantly above background.

A field test of a system rated for use in hazardous atmospheres was performed in near offshore Louisiana in August 1995.

The system was assembled, tested, and the background count rate recorded. A comparison of the background count rates on the workover barge and in the laboratory is shown in Figure 7. The average laboratory background rate is about 85 counts/second. The background rate on the barge averaged about 18 counts/second. This reduction in count rate is expected since most background counts are due to small amounts of radioactive material in the soil.

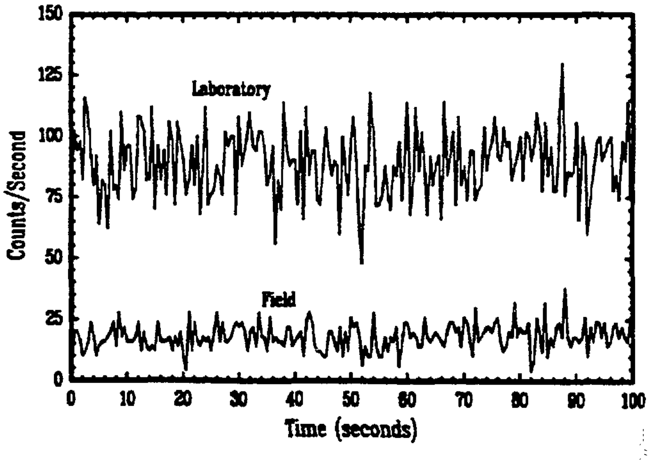

Figure 7 Background Count Rate

For the field test, the explosion proof enclosure containing the detector was installed on the bell nipple above the BOP's. Figure 8 shows the installation of the detector system. The enclosure was installed as close to the

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nipple as possible. This placed the detector about 8 inches from the center of the tubing being pulled.

The closer the detector is placed to the tubing and the less material there is between the detector and the tubing being pulled, the more sensitive the system will be to low levels of radioactive contamination.

In this installation, the bell nipple was filled with brine. The detector would have been more sensitive if the detector was installed on the bell nipple above the brine.

Figure 8 Response from Gas Lift Valve

This well was selected for the tests because:

1. This field has a history of NORM problems and
2. This well had produced a large amount of water since it was last worked over.

Thus, the tubing in this well was expected to be contaminated with NORM.

During pulling operations, the packer refused to release from the bottom of the tubing string. Thus, the pulling rate was limited to 2400 ft/hr to prevent significant reduction of the hydrostatic head in the well and possibly cause gas incursion into the well.

No NORM contamination of the tubing was detected. However, NORM contamination was detected in the bottom four gas lift valves. The contamination in each valve caused a reading of less than 30 μR/hr. This level was detectable with this system even though it is less than 20 μR/hr above background.

The contaminated gas lift valves were detected because I was watching the computer display during pulling operations. I am not sure this low level of contamination would have been detected if the pulling rate had been greater than 10000 ft/hr since an alarm level low enough to detect this level of contamination would result in several false alarms.

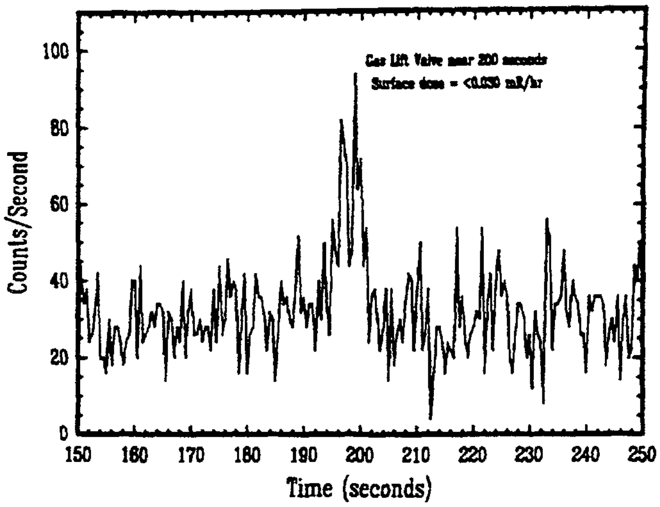

Figure 9 Response from Gas Lift Valve

In most applications, if the detector can be positioned no more than 8 inches from the tubing and there is less than 1/2 inch of steel between the detector and the tubing, contamination levels of 50 μR/hr can be detected with a properly operating/adjusted system similar to the one tested.

CONCLUSIONS

- Sodium iodide crystals of 3 × 3 inch and larger can be used with an alarming ratemeter to detect NORM contaminated tubing. Smaller crystal detectors may be able to detect contaminated tubing if they are positioned within 5 inches of the center of the tubing.
- The detector can be placed inside an aluminum explosion proof enclosure and still detect contaminated tubing.
- To increase sensitivity, the detector should be positioned so the face of the detector is as close as possible to the center of the borehole. Tests have shown that distances of less than 8 inches are acceptable if there is little steel between the tubing and the detector.

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- The amount of material between the detector and the tubing being pulled from the well should be kept to a minimum to improve system sensitivity.

- The response time of the ratemeter alarm circuit should be about one second. Faster response times will increase error rates and response times of 3 seconds or longer may not allow low levels of contamination to be detected at high pulling rates.

- Shielding of the detector will decrease the background count rate and thus improve the signal to noise ratio. That will improve the ability of a system to detect low levels of contamination.

For installations where:
1) the pulling rates are high,
2) the detector must be placed over 8 inches from the center of the tubing,
3) there is more than a 1/2 inch of steel between the tubing and the detector, or
4) the tubing is large or casing is being pulled,

tests should be performed to determine if this system can detect down to the regulatory limit or if a system with a larger detector or multiple detectors would be required to detect low levels of NORM contamination.

Tests will need to be performed in each field to determine the proper alarm level setting for detecting contaminated tubing. Since background counting rates, tube pulling rates, and installation configuration will vary from field to field and rig to rig, the proper settings for each installation must be determined. A suggested starting alarm level is 1-1/2 times background count rate for onshore installations and 2 times background for offshore installations..

ACKNOWLEDGEMENTS

I wish to thank Mr. Ralph Harding for requesting this device and for his support during the first field test of these systems. I also wish to thank Mr. Charles Brooks for arranging for the second field test and the assistance of the workover crews during the field tests. The field test would not have been a success without their help.

My thanks also go to Dr. I. R. Supernaw for his suggestions during the selection and laboratory testing of these devices.

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HIGH DENSITY RADIOLOGICAL SITE CHARACTERIZATION SURVEYS FOR NORM SITES

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Abstract

A continuous (1 sample/sec) walkover radiological survey was performed over 13.4 hectares of open and wooded, NORM-contaminated terrain. Data from a near-surface NaI detector, and either a second NaI detector or a dose rate meter at one meter above the surface, were recorded at each sampling location along with the position coordinates. The position coordinates were automatically determined each second to an accuracy of 15 cm using an ultrasonic time-of-flight technique.

Introduction

The radiological surveys were conducted on three sites. Site A contained active and inactive oil wells, piping runs and pipe storage areas. Site B was the location of a pipe descaling operation, two oil storage tanks and an unregulated public dumping area. Site C contained three standing storage tanks, one destroyed tank, fields in which the descaled piping was used for fencing, farm buildings and ponds. The topography of these sites was generally flat with some hills and slopes.

Survey System

The radiological survey was conducted using Chemrad's USRADS® System interfaced to two scintillation detectors and a dose ratemeter. The scintillation detectors were Ludlum Model 44-2 Sodium Iodide (NaI) probes (2.54 cm x 2.54 cm) connected to Ludlum Model 3 ratemeters. The dose ratemeter was the Bicron MicroRem meter.

The USRADS System consisted of a Data Pack, Stationary Receivers, a Master Controller and a portable personal computer. The Master Controller and the computer system

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were mounted in a utility vehicle which was positioned near the survey area. The Data Pack and the detectors were carried by the surveyor. The Data Pack contained the interface circuitry for the radiological survey instruments, the ultrasonic transmitter, and radio frequency (RF) equipment to establish two-way communication with the Master Controller. A handheld terminal was also connected to the Data Pack to allow the surveyor to remotely interact with the computer. The surveyor also carried a two-way radio for voice communications with the computer operator.

Independent of the USRADS Survey, an attempt was made to use a differential global positioning system (GPS) to survey the same areas. This system proved to be satisfactory for surveying open areas, but incapable of operating suitably for walkover surveys in woods or around structures where the view of the sky was obstructed. Unfortunately, the contaminated locations were most often in these obstructed areas, so the use of the GPS system was discontinued.

System Operation

Each second the Data Pack transmitted the radiological survey data from all three detectors to the computer via the RF link. At the beginning of each one second interval, the ultrasonic crystal mounted on the surveyor's backpack was pulsed by the Data Pack. The Stationary Receivers measured the time taken for this pulse to reach each of them. Each Stationary Receiver relayed a stop signal to the Master Controller via an RF transmission upon receiving the ultrasonic signal.

Through this process, the distance of the surveyor from each of the Stationary Receivers was determined using the measured speed of sound. The computer then calculated the location of the surveyor relative to the Stationary Receiver locations and stored the radiological survey data with that location. The location of the surveyor and the radiological survey data were plotted on a grid map that was shown on the computer's display in real time. The computer operator performed an on-line quality assurance inspection that the survey was being conducted according to the prescribed protocol, that the detectors were performing properly, and that the findings were reasonable. Any deviations from these conditions were immediately investigated and corrected. Once proper survey coverage has been accomplished, the operator has the choice of several software routines to assist in the identification of anomalies or other items of interest.

The number of Stationary Receivers deployed depended on the size of the area to be surveyed, the topography of the site, and the presence of woods or structures. Up to thirteen Stationary Receivers were used on sites as large as 100 m x 100 m. The time taken to setup the USRADS System and complete the survey of these larger sites would require as much as three hours, particularly if the site contained steep terrain or woods.

Survey Protocol

The standard survey protocol called for one NaI detector to be swung back and forth in

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front of the surveyor while being held approximately 15 cm above the ground. The second NaI detector and the dose ratemeter were carried approximately 1 meter above the surface.

To the extent physically possible, the surveyor walked over the site along parallel lanes separated by 1 to 1.5 meters at a pace of approximately .75 meters/sec. This typically provided over 8,000 sample locations for each detector within a 100m x 100m area.

Areas in which elevated activity was detected were further surveyed by repeating the above protocol in a cross hatched pattern.

In addition to the walkover survey, one minute stationary biased samples were collected at designated locations. These were the locations of highest readings within an area, or positions at which manual readings had previously been taken using a Pressurized Ion Chamber (PIC) at 1 meter above the surface to determine the radiation dose rate. If the USRADS Survey was performed prior to the PIC readings being made, then the USRADS biased locations were marked with flags so that PIC readings could subsequently be made at the same locations.

Results

The designated areas were successfully surveyed according to the prescribed protocol, including wooded areas and around buildings and structures. Preliminary data presentations for each day's work were used to perform QA/QC on the data, to review the survey's progress, to consider the significance of any findings, and to direct the subsequent day's activities. Daily deliverables included color track maps showing each detector's position and readout by color levels each second.

Hot spots found during the survey were later successfully relocated using the maps produced. Some of the surveys showed contaminated areas outside of areas previously remediated. The USRADS System produced maps defining the areas that were above release levels.

Final deliverables included a consolidated track map showing surveyor coverage (consolidated for an entire site) and consolidated color contour maps showing the radiation findings as isopleths of constant intensity for each detector. The final data presentations, including the final version of the daily deliverables, were delivered within two weeks following the completion of the survey.

Examples of the deliverables are shown in Figures 1-8. Figures 1 and 2 show the color track maps for the NaI detectors at 15 cm and 1 meter above the surface, respectively, for the survey of OW1 Site. Figures 3 and 4 show the respective color contour maps for this area. Note that the contamination is located on a service road adjacent to the well where it can easily be transferred onto the wheels of vehicles.

Figures 5 and 6 show the corresponding track maps at the OW52 Site, while the color

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contour maps are shown in Figures 7 and 8. Of significance in these maps is the finding of a hot area in the northern portion of the area surveyed. This area was on the edge of a washout, suggesting that part of the contaminated soil may have eroded downhill. Also noteworthy was the finding of a small hot spot near the middle of the surveyed area which was an isolated concentration of activity in an otherwise clean area.

Conclusions

The USRADS Radiological Survey was highly successful in accurately and cost effectively locating radioactive hot spots and measuring the radiological dose rate in all terrains, including woods and around structures. Clean areas were also thoroughly documented.

The GPS positioning technology was shown to work satisfactorily, but with somewhat poorer positional resolution, in open areas, but did not work in wooded areas or around structures.

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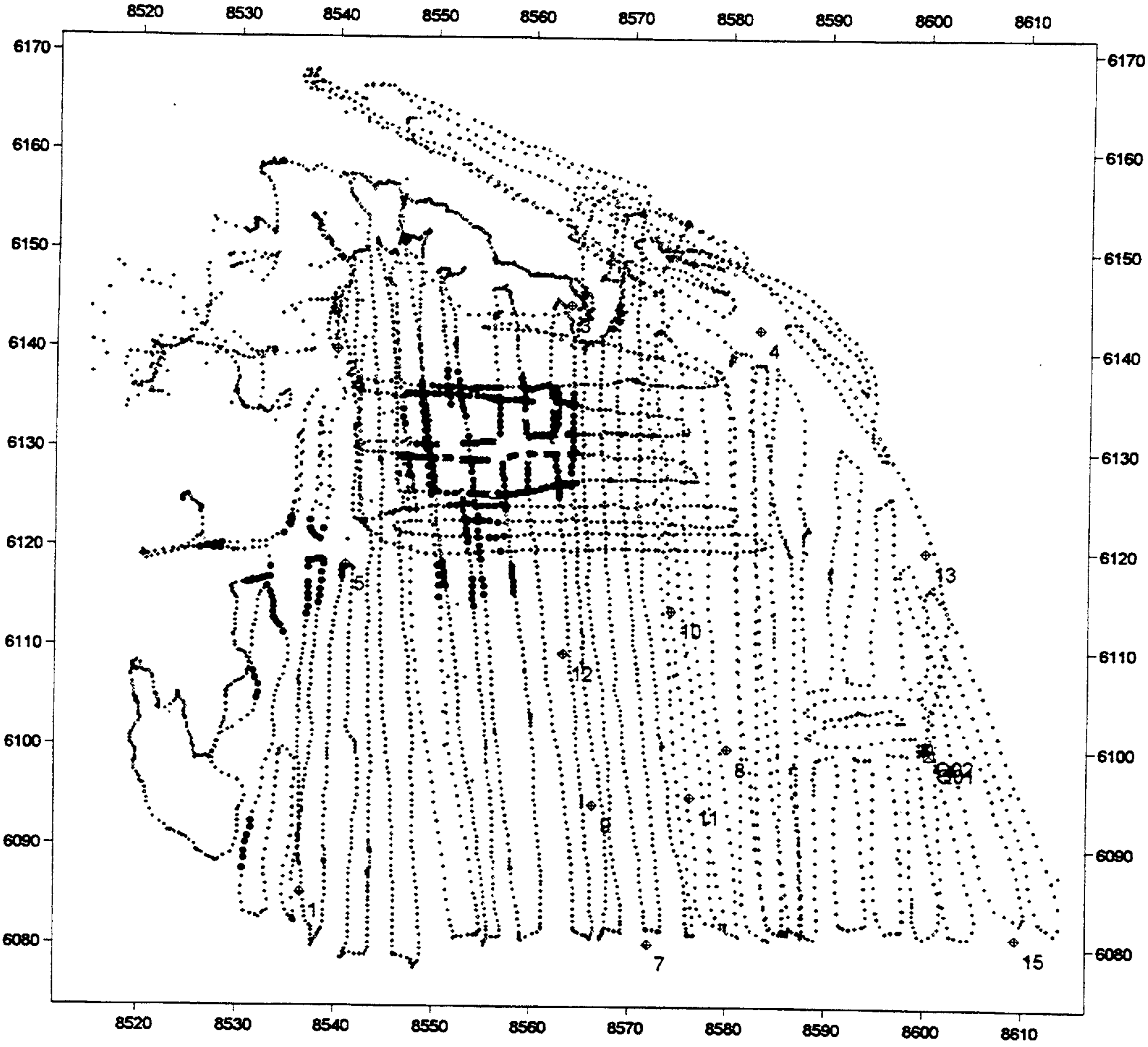
USRADS v1.46e Track Map

Site: OW1 (A) **Signal: NaI (CPM)** **Time: 13:00:59 05/24/95**

Threshold:
> 15161 •

< 2000	■	**20000 to 50000**	■
2000 to 5000	■	**50000 to 100000**	□
5000 to 10000	■	**> 100000**	■
10000 to 20000	■		



9405.5478

Figure 1.

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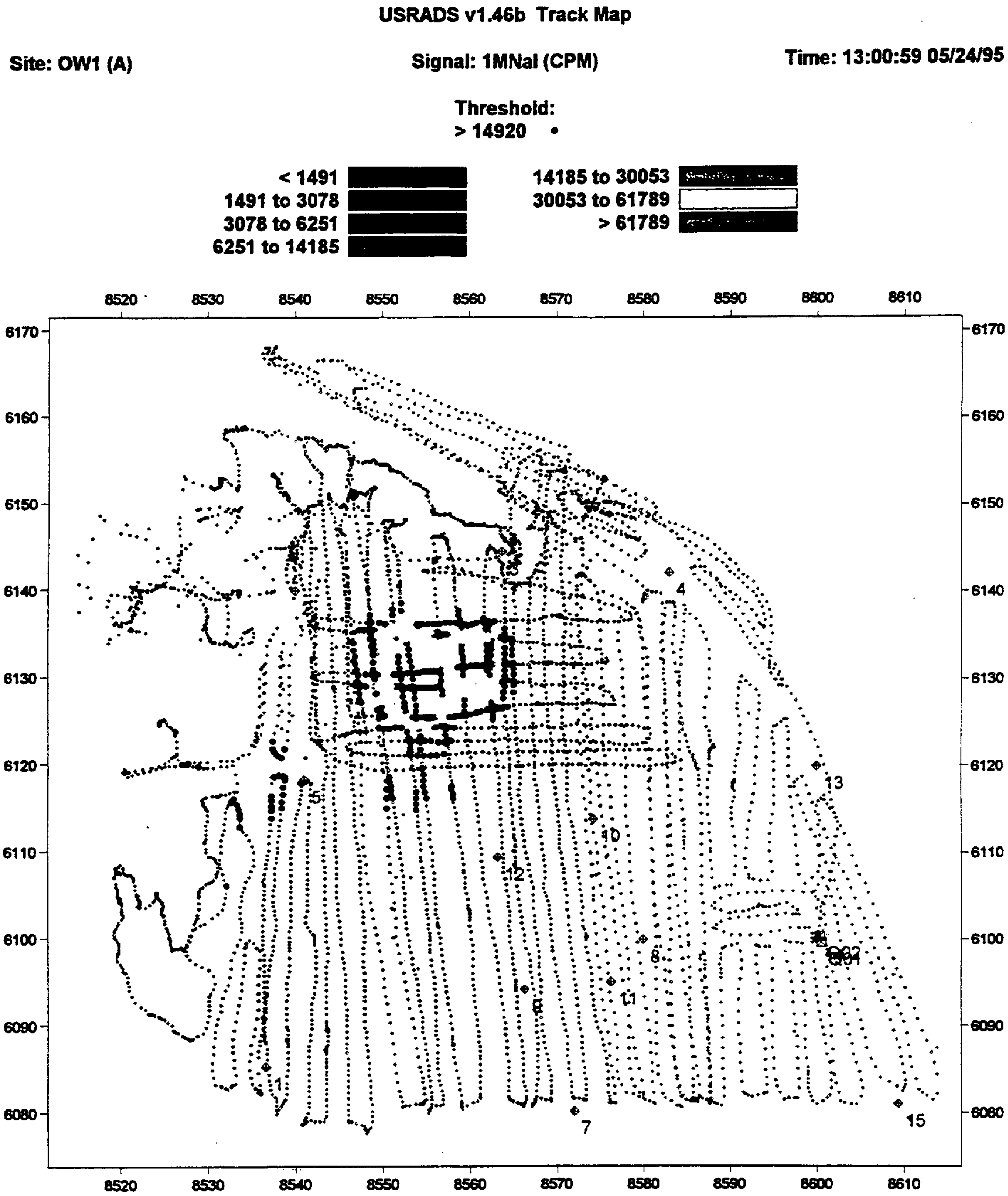

9405.8060

Figure 2.

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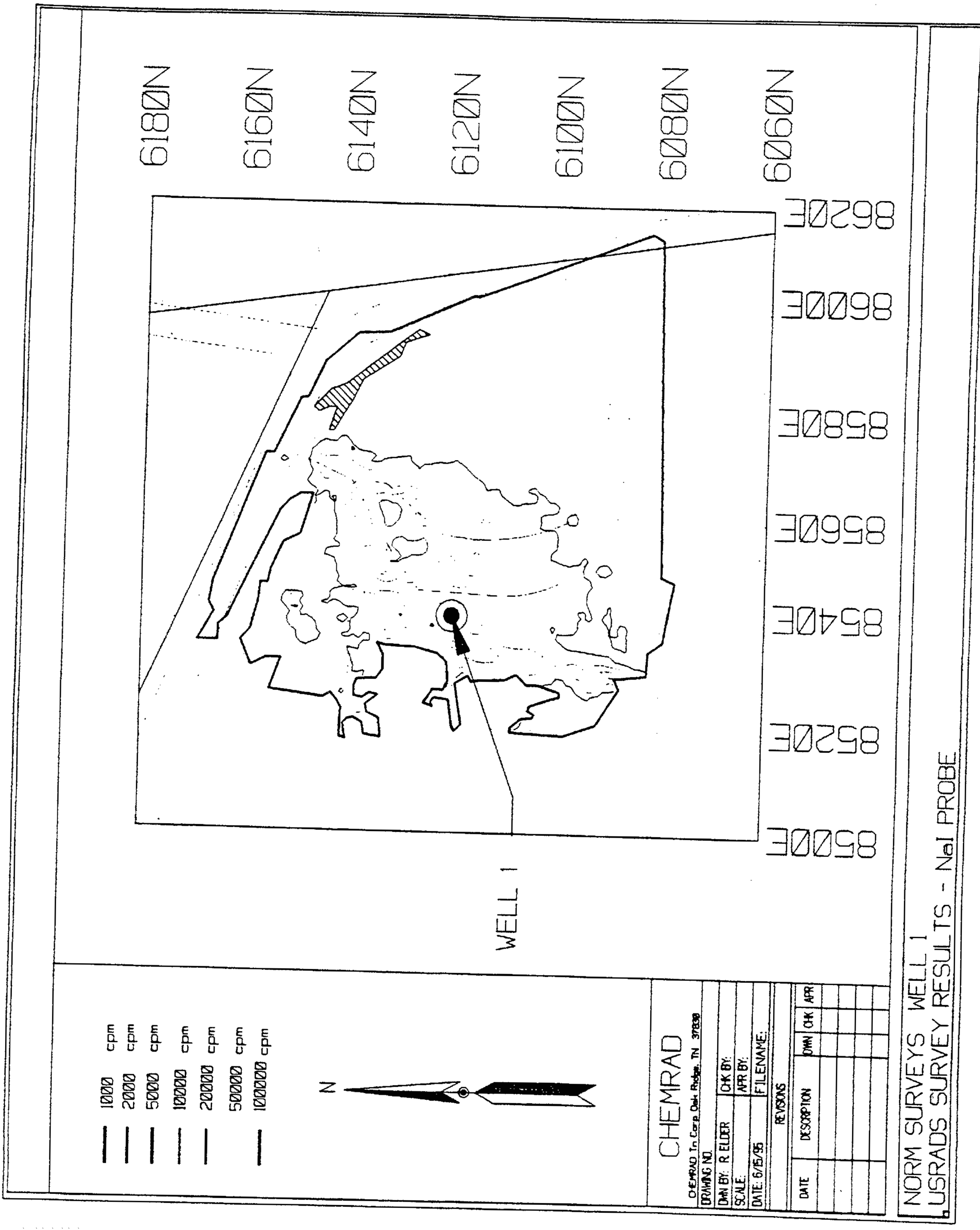

Figure 3.

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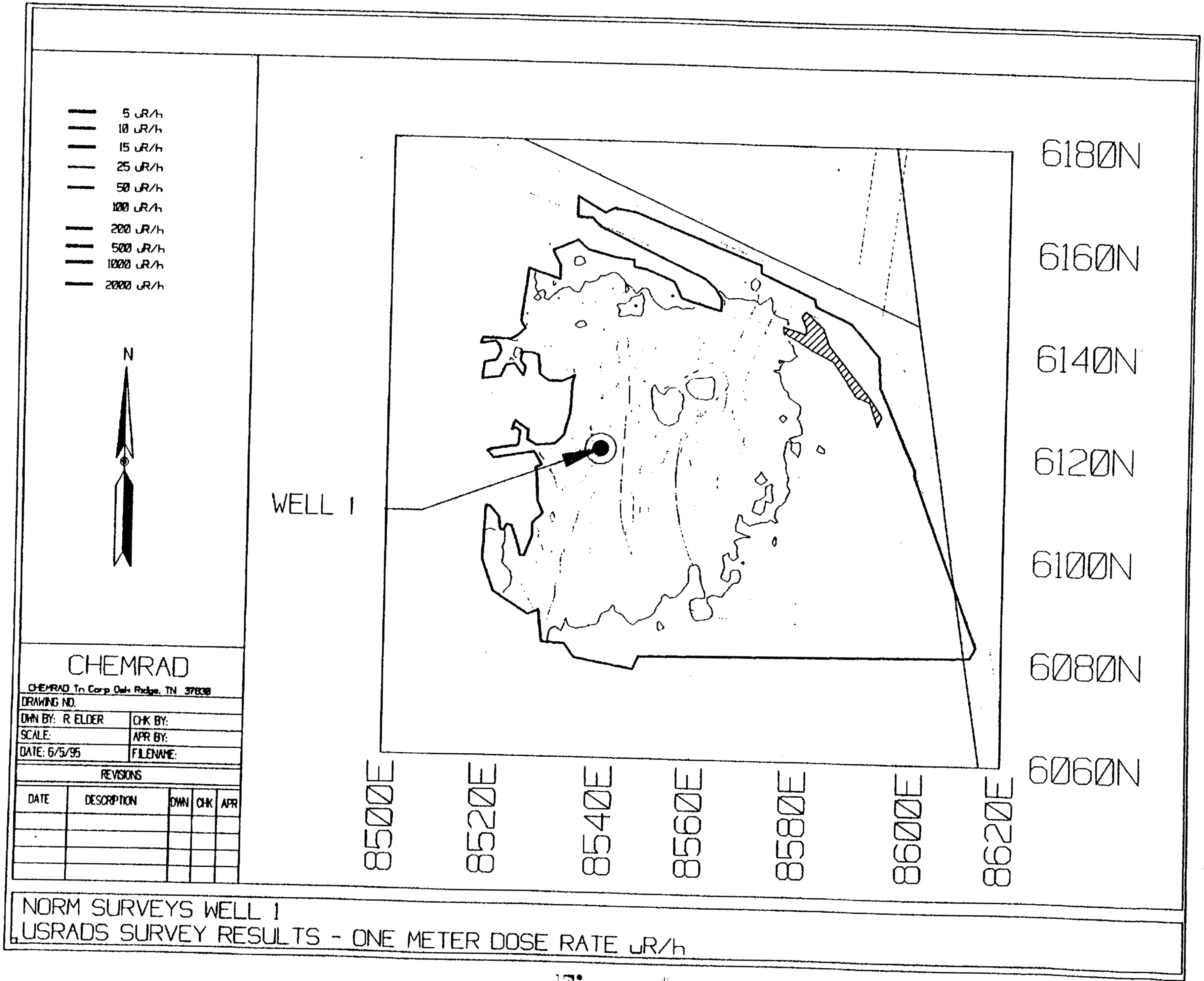

Figure 4

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USRADS v1.46e Track Map

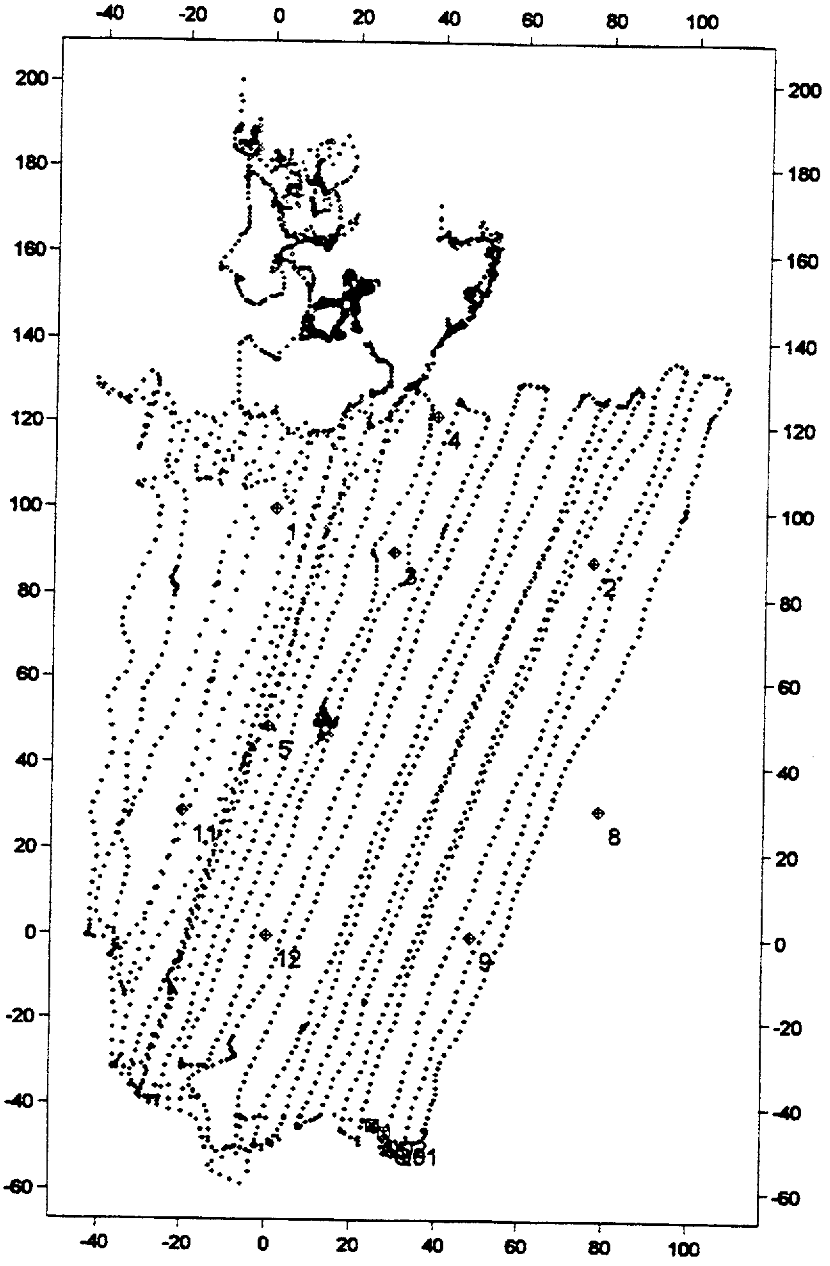
Site: OW52 (A)

Signal: NaI (CPM)

Time: 09:58:29 05/24/95

Threshold:
> 13121 •

< 2000	■	20000 to 50000	■
2000 to 5000	■	50000 to 100000	□
5000 to 10000	■	> 100000	■
10000 to 20000	■		



9402.9224

Figure 5.

1 of 1

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USRADS v1.46e Track Map

Site: OW52 (A) **Signal: 1MNaI (CPM)** **Time: 09:58:29 05/24/95**

Threshold:
> 5415 ●

< 1491	■	**14185 to 30053**	■
1491 to 3078	■	**30053 to 61789**	□
3078 to 6251	■	**> 61789**	■
6251 to 14185	■		

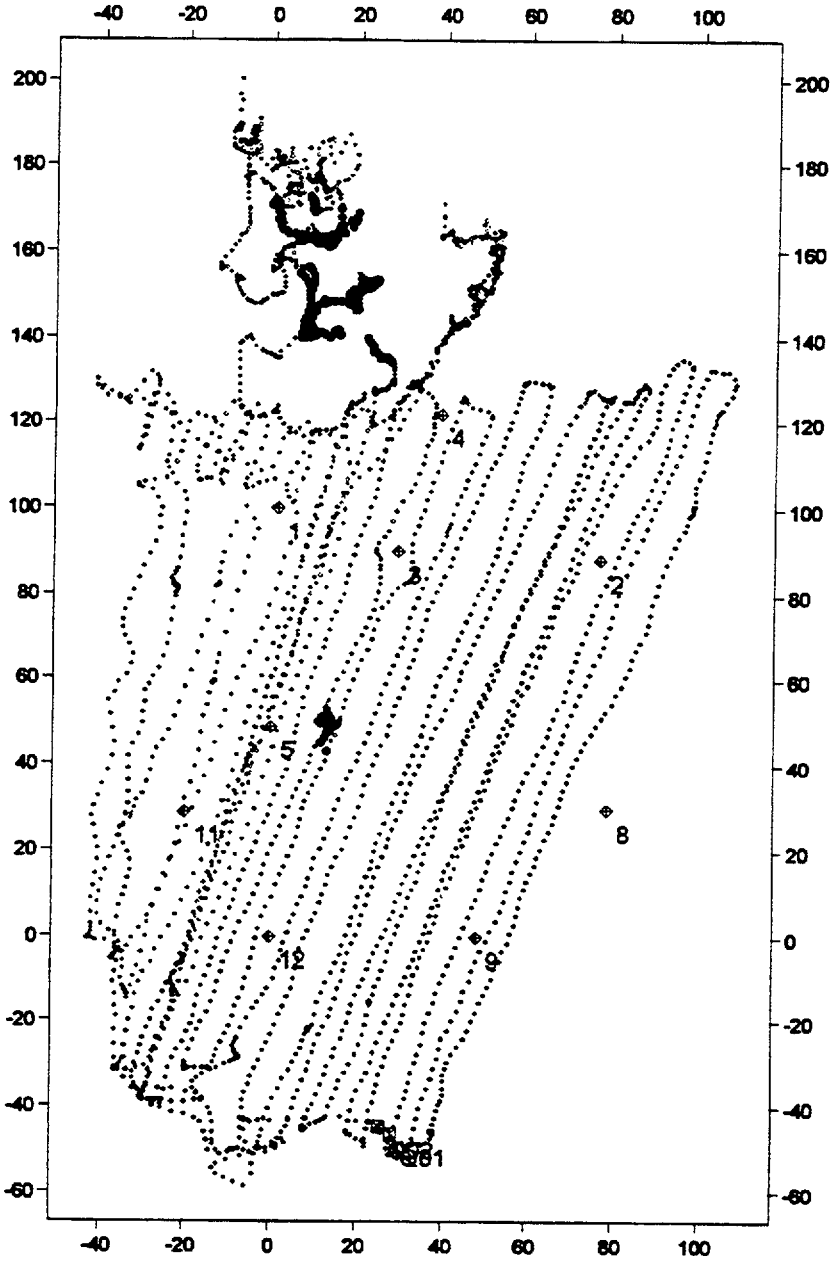

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Figure 6.

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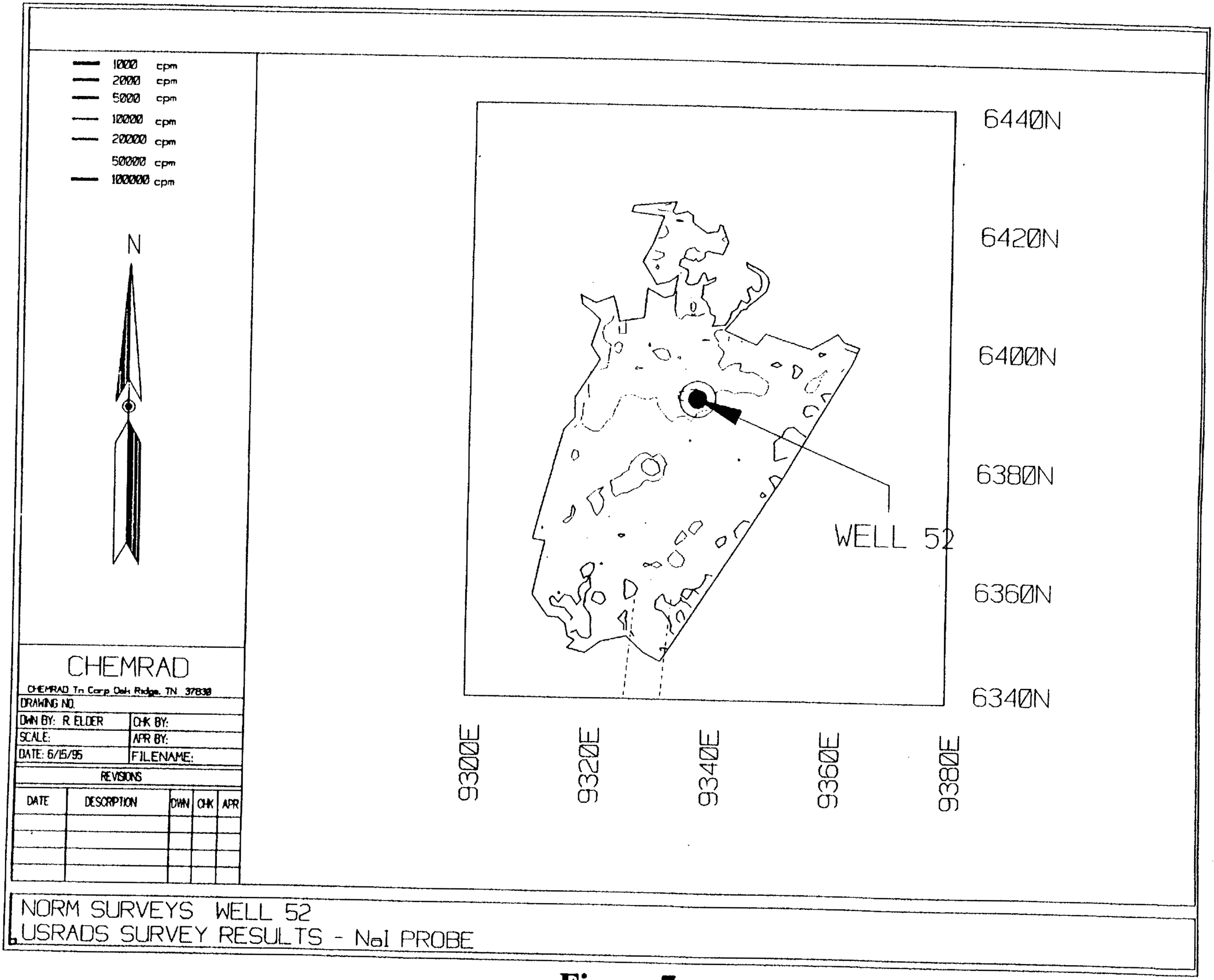

Figure 7.

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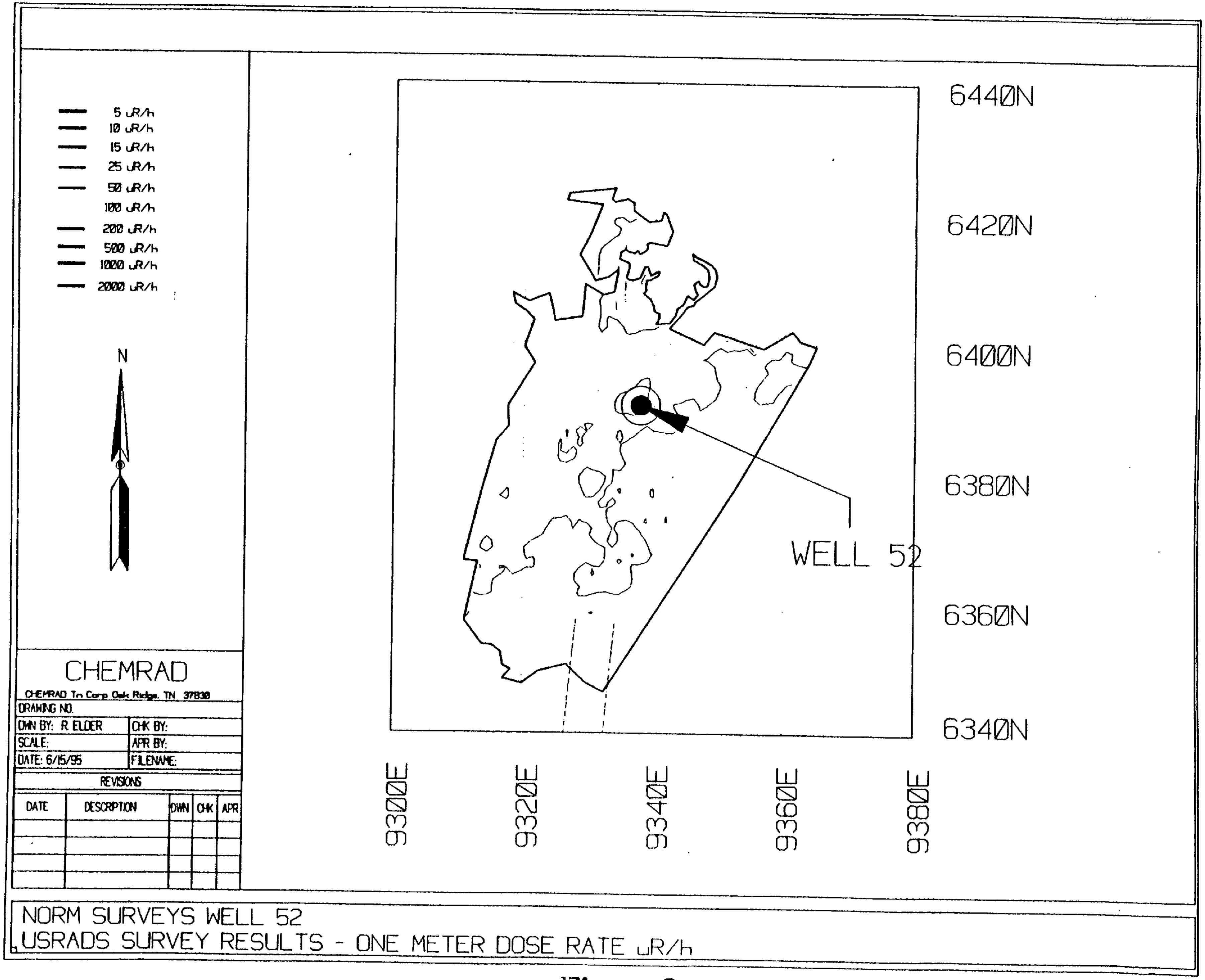
5 uR/h
10 uR/h
15 uR/h
25 uR/h
50 uR/h
100 uR/h
200 uR/h
500 uR/h
1000 uR/h
2000 uR/h
N
6440N
6420N
6400N
6380N
6360N
6340N
9300E
9320E
9340E
9360E
9380E
WELL 52
CHEMRAD
CHEMRAD Tn Corp Oak Ridge, TN 37830
DRAWING NO.
DWN BY: R ELDER
CHK BY:
SCALE:
APR BY:
DATE: 6/15/95
FILENAME:
REVISIONS
DATE
DESCRIPTION
DWN
CHK
APR
NORM SURVEYS WELL 52
USRADS SURVEY RESULTS - ONE METER DOSE RATE uR/h

Figure 8

Methods of Estimating Dose to Individuals from NORM

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Abstract

Dose from NORM for occupational situations does not require methods and techniques different from other ionizing radiation situations. In some case additional care is necessary since the radiations cannot be distinguished from background, except for intensity.

The regulations concerning occupational dose from NORM are 10 CFR 20 and 29 CFR 1910.96 In order to show that no radiation protection program is required under either of these regulations, careful measurements with compensated instrument readings may be necessary, as well as, a good definition of the local background. Dosimetry devices may be required for a radiation protection program and could be very useful in demonstrating no need for a radiation protection program.

The regulations governing occupational dose also require controlling public dose. Public dose must be considered in a radiation protection program.

Risk calculations for occupational situations may be required under RCRA and CERCLA, although there is no clear regulatory basis for the risk calculations. Such calculations require attention to detail if risk limits are approached. Knowledge of the background is essential and measurements should be made at actual work locations. Dosimetry devices may be useful, but measurements must be well controlled.

Introduction

Ionizing radiation dose to individuals in occupational situations is covered by 10 CFR 20 or 29 CFR 1910.96. Both these regulations limit dose to individuals to 5000 mrem/y (50 mSv/y) and require a radiation protection program when it is expected that any individual may obtain an annual dose in excess of 500 mrem (5 mSv). These annual doses are summed from all methods of exposure at the work place, external and internal. In general, members of the public should not receive in excess of 100 mrem/y (1 mSv/y). Few cases of occupational or public dose from NORM are explicitly covered by 10 CFR 20. The language of 29 CFR 1910.96 incorporates, by reference, 10 CFR 20 for all industrial situations not applicable under 10 CFR 20. Therefore, industrial uses of NORM are regulated with respect to dose to individuals under 29 CFR 1910.96. This is hardly an undisputed interpretation.

Additional and specific regulation of some forms of NORM can be found in NESHAPs. Based on the classification in NESHAPs of NORM as a hazardous substance, further regulation of NORM is possible under language in RCRA and CERCLA. This interpretation is also a source of dispute. Regulation under NESHAPs, RCRA, or

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CERCLA may depart from dose as a limit and use life-time risk as a limit. Depending upon the exposure period, a life-time risk of 10^{-4} may result in an annual dose far less than 100 mrem (1 mSv).

The dose range of interest, up to 5000 mrem/y, less than 500 mrem/y, less than 100 mrem/y, or less than a life-time risk of 10^{-4}, present differing problems in individual dose measurement. Not surprisingly, the difficulties increase with decreasing dose.

We discuss methods and problems of external dose measurement based on experience in several types of facilities where NORM was encountered. These cases include metal and rare earth extraction, water treatment, phosphorus and phosphate extraction, lithium extraction and processing, and a plant disposing of NORM contaminated materials, where NORM was used in construction of the facilities. Internal dose was also a concern at most of these facilities, but internal dose will not be covered.

Dose Estimation Methods

Occupational Dose

The occupational category under 10 CFR 20 and 29 CFR 1910.96 require measurements to estimate doses from 0 to 5000 mrem/y or measurements to ensure that doses will be less than 500 mrem/y. These dose ranges are those of the nuclear and medical communities and have a long history of measurement. There are many standard techniques for dose rate and time estimates of dose or direct dose measurement using dosimetry devices. Doses can also be modeled based on concentrations of radionuclides and shape of the source. There are few problems with accuracy with any of the available techniques until limits are reached, either 5000 or 500 mrem/y or some other administrative limit.

The accuracy problems are associated with defining background and non-linear response of devices and instruments in the measurement of background and NORM. The problems occur with over-response rather than under-response. The response problems occur because calibrations are usually made at only a single energy rather than a spectrum of energies typical of NORM and the devices usually have an energy dependent response, which may preclude correct calibration under any circumstance.

At typical sites of the nuclear and medical communities, only a few locations account for the dose to workers. Dose rate measurements in these cases range upward from a few to tens of mrem/h. Standard dose rate instruments easily measure these dose rates. If the radiation field is not localized, but general, exposing the worker at all or nearly all time, then a dose rate of 0.25 mrem/h for 2000 h would constitute the annual dose limit. A dose rate this small or smaller strains the reliability of standard instruments designed to read in mrem/h. More sensitive instruments, designed to read in μrem/h are required.

Dosimetry devices are usually required to measure dose when a radiation protection program is required. Standard dosimetry devices should have few limitations in the region

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of dose from 500 to 5000 mrem/y. Two important variables must be considered, time of exposure and storage background for the device, although non-linear energy response may be critical in some cases. Nevertheless, most programs are straight-forward, unless dose limits are approached. If there is a possibility of exceeding dose limits, a program for controlling dose should be used before refining the dosimetry process.

Public Dose

When there is a consideration of occupational dose, 10 CFR 20 and 29 CFR 1910.96 require consideration of public dose. The public category of dose for a limit of 100 mrem/y is, almost always, calculated. The calculation is usually conservative, based on a Reasonable Maximum Individual. Dose can be measured using dosimetry devices and sensitive recording instruments at typical public locations. These measurements are usually performed in conjunction with a calculation of dose. Measurements are acceptable as the only method of dosimetry.

Some type of measurement is necessary for calculating dose, whether the measurement is of dose, dose rate, or concentration of radionuclides. The Reasonable Maximum Individual is determined at the 95 percentile of the propagated uncertainty of measurements and time estimates. It is often necessary to reduce the uncertainties by increasing the number of measurement locations and the measurement accuracy. Standard techniques are usually available for making environmental measurements for dose calculations.

Risk Calculations

Dose measurements to support RCRA or CERCLA do not apply to occupational situations according to 29 CFR 1910.96, but risk assessments for outdoor occupations on sites where there is RCRA or CERCLA activity have been made. Workers assessed were not involved in the RCRA or CERCLA activity. To date no consequences have resulted from such risk assessments of which the authors have knowledge, since the risks were found to be 10^{-4} or less. Considerable effort was required to obtain an accurate risk assessment. Accuracy was achieved by basing the calculations on appropriate measurements at appropriate locations.

Dosimetry

Dosimetry is an attractive method of measuring individual dose since it is specific to an individual. There is no need to perform calculations or dose rate measurements. If additional information is necessary, such as the location where the dose was received, additional measurements are necessary since the dose is specific to the individual, not the location. Transit and storage dose must be subtracted from the total dose to obtain individual dose. Storage dose is dose received by the dosimeter for times not worn by the individual. Storage time usually exceeds wear time by a factor of 2 or more. Transit dose is the dose received between the storage location and the dosimeter processing location. Transit dose for remote processing facilities can equal the storage dose. Storage and transit dose can usually be obtained from control dosimeters. These 2 subtracted doses

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become more important as the individual dose decreases and the time to measure the dose increases.

The time to measure the dose is dependent upon the accuracy and sensitivity required for the dose estimate. Doses that are clearly different from background can be measured in a short time with acceptable accuracy. Doses down to 100 mrem/y can be measured in a three month exposure. Smaller doses require considerable care for the transit and storage doses and up to a year of exposure. Figure 1 shows measurements made with Al_2O_3 dosimeters in a attempt to measure as low as 10 mrem without particular control of the storage dose.

The figure shows measurements made at 2 dose rates, 20 and 40 µrem/h. The intercept of the 2 lines is 12.5 mrem and is the sum of the storage and transit doses. The horizontal line at 22 mrem is the detection limit based on 5 dosimeters at the storage location. The results show that at the lower dose rate of 20 µrem/h over 400 h or 10 weeks of exposure are necessary for a detectable difference from background. The higher dose rate of 40 µrem/h was detectable in less than 200 h or 5 weeks. Based on this analysis, at least, 3 months would be required to obtain acceptable accuracy at the higher dose rate (Currie 1978).

In a test where the dosimeters were worn by individuals, the control on the wear time and storage dose was sufficient for a detection limit of 30 mrem or 3 times the static test. Further tests were performed for better storage control in a low background area. A detection limit of 15 mrem was found to be achievable.

Dose Rate

Dose rate is the most popular method of estimating dose, because it is immediate and identifies the source. The major drawback is that good estimates of the time of exposure and the position of exposure are necessary. For occupational doses reportable under 10 CFR 20 and 29 CFR 1910.96, dose by a dosimetry device is usually required. Dose rate measurement and a conservative calculation is sufficient to show that a radiation protection program is not required because doses are less than 500 mrem/y.

The accuracy of dose rate measurements may be critical when limits are approached. It may be necessary to reduce conservatism. Conservatism can be reduced by converting over-responding instruments using an equation that converts the calibration conditions to the NORM conditions. Additional removal of conservatism may be gained by converting to equivalent dose based on the geometry of the NORM source (EPA 1993, ICRP 1987, Zankl 1992).

Conversion of instrument response to NORM conditions requires knowledge of the NORM dose rate at various locations for comparison to the instrument reading at the same locations. Pressurized ionization chambers (PIC) are energy independent over the range of background and NORM energies (Beck 1971). It is accepted as the standard for

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dose in air for human dose measurements. Other types of ion chambers and compensated GM detectors may also be adequate but should be compared to a PIC under the conditions to be measured. Tissue equivalent plastic scintillation detectors can be very close to NORM dose rate, requiring no conversion.

The conversion of the dose rate is usually more important at the lowest dose rates. Measurements of low dose rates are more likely to require conversion, not because of the energy mixture at low dose rates, but because most low dose rate instruments are chosen for their sensitivity. In other words, a high response at low dose rates usually means over response. Detection of radiation in some cases may be more important than correctly measuring it. A popular instrument for low dose rate measurements is the sodium iodide scintillation detector. The usual calibration of this instrument results in over response for low energies and under response for high energies. For NORM, this means over response. Attempting to adjust the response for certain conditions is usually not advisable, unless it is known that use will be restricted to only those conditions.

The sodium iodide readings can be converted to PIC equivalents by comparing to a PIC over a range of dose rates, then regressing the sodium iodide readings against the PIC readings. The result is

$$\mathrm{PIC} = a(\mathrm{NaI}) + b,$$

PIC is the PIC equivalent, NaI is the sodium iodide reading, a is a constant less than 1 and b is a constant greater than 1. The authors have found that *a* is usually near 0.6 for all locations and *b* is usually equal to the cosmic dose rate. The constant *b* is, therefore, altitude dependent. The generality of this equation allows for easy conversion without extensive measurements, but should always be confirmed in critical situations.

Geometric compensation for equivalent dose may also be necessary to eliminate conservatism. The PIC is designed to measure dose in air, which can usually be converted to dose in tissue at 1 cm depth by multiplying by 0.96 (Beck 1971). This conversion is not sufficient for conversion to whole body dose for all energies since equivalent dose must be calculated for internal organs(EPA 1993, ICRP 1987, Zankl 1992). The geometry of the source must also be considered since the organs are differently irradiated from different directions. Figure 2 shows the energy dependent conversion for a body standing on an infinite planar source. For the usual energy spectrum for NORM, the PIC conversion factor for the planar source is 0.65.

Measure or Model

For annual doses down to 500 mrem/y it may be required that doses be measured using dosimetry devices, but that dose rates be measured at locations for purposes of posting and designing a radiation protection program. From 500 to below 100 mrem/y a combination of measurement and calculation may be possible, depending upon the accuracy or need to demonstrate protection is adequate by conservative estimate. As

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doses become more critical, a more exacting measurement program may be necessary. If occupational doses become limited by RCRA or CERCLA risk estimates, careful measurement and exacting calculations may be necessary.

Measurement for the lower dose regions may be limited by the choice of instrument or dosimetry device. The lower the dose, the more sensitive the instrument or device, inviting over response. Important to low dose measurements is correctly measuring the background and the range of background. It may be important to know the local background for a given measurement rather than the general background for the area. Figure 3 shows a probability plot for background in a region where NORM measurements were made. Knowing the local background in this case can be very important, especially if dose rates on the order of 10 µrem/h are important. Observe from the figure that 2 straight lines can be fitted to the data, indicating 2 different background areas. The area comprised both a volcanic flow and alluvium.

Modeling in this case must also consider this differing background. Models may only allow an average background, considering all dose rates above the average to be from the NORM source. Common models also may use the highest source dose rate for a location rather than the average for the location. Models may also discount shielding and maximize the time of exposure. The inherent conservatism of some models is acceptable, as long as the doses calculated are below the imposed limits. When limits are exceeded, then a more careful evaluation of the dose is necessary.

When limits are exceeded in a modeled dose, conservatism must be eliminated. Conservatism is inherent in most models, but often, the model can be improved by improving the measurements and by performing measurements representative of the work situation. In a case involving the authors, risk was modeled for occupational doses at CERCLA sites. The first risk calculation was based on dose rates calculated from the NORM concentration at selected locations. It was assumed that these concentrations were representative of other locations.

When the calculated risk easily exceeded life-time risks of 10^{-4}, dose rate measurements were requested for the same locations where dose rate was calculated from the concentrations. The dose rate measurements were performed with a GM detector without compensation for the over-response. The dose rates measured were found to be equal to or higher than the calculations. Since the locations used for the calculations and measurements were not typical of occupational locations, measurements from other locations were used to obtain average dose rates for areas of the sites. These additional measurements were previously performed under NESHAPs and/or RCRA. These measurements were made with an NaI scintillator, were also not made at occupational locations, and did not appreciably alter the risk assessment.

A series of measurements were made in occupational locations and in occupational situations (shielding) using a PIC and a tissue equivalent plastic scintillator. The majority of the occupational time was spent in vehicles, heavy earth moving equipment, or in

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equipment control rooms. Figure 4 shows the results of some of these measurements. At each position measured, the total unshielded, total shielded, and net (above background) dose rates are shown. The net dose rate is the quantity necessary to calculate occupational risk. Once actual, net dose rates are known, the life-time risk can be calculated. The calculation for each occupation is performed as follows:

$$\text{Risk} = \text{RF} \times \text{DA} \times \text{WY},$$

where

RF = risk factor
DA = annual dose
WY = years of work.

Annual dose is

$$\text{DA} = \Sigma(\text{NDR}_i \times \text{ET}_i \times \text{EF}_i),$$

where

NDR = net dose rate (average for the location)
ET = exposure time in hours per day
EF = exposure frequency in days per year.

At this point in the calculation, the uncertainties can be propagated for determination of a Reasonable Maximum Individual. Often, in the name of conservatism, a Reasonable Maximum Value is calculated for each term, which greatly inflates the calculated risk. In the CERCLA risk calculations for these sites Reasonable Maximum Values were used, but the use of net dose resulted in life-time risks of less than 10^{-4}. Calculation of equivalent dose, which was not done in these cases, would have further reduced the calculated risk.

Conclusions

Compliance with 10 CFR 20 and 29 CFR 1910.96 can be accomplished with standard equipment and methods for radiation protection programs. Care must be taken as limits are approached that instrument readings are properly compensated. When it can be shown that no radiation protection program is required under either of these regulations, careful measurements with compensated instrument readings may be necessary, as well as, a good definition of the local background. Dosimetry devices may be required for a radiation protection program and could be very useful in demonstrating no need for a radiation protection program. It may be necessary to convert doses if the dosimetry devices over-respond to NORM.

Risk calculations for occupational situations under RCRA and CERCLA require attention to detail if limits are approached. Knowledge of the background is essential and measurements should be made at actual work locations. Dosimetry devices may be useful, but storage and transit doses must be well controlled.

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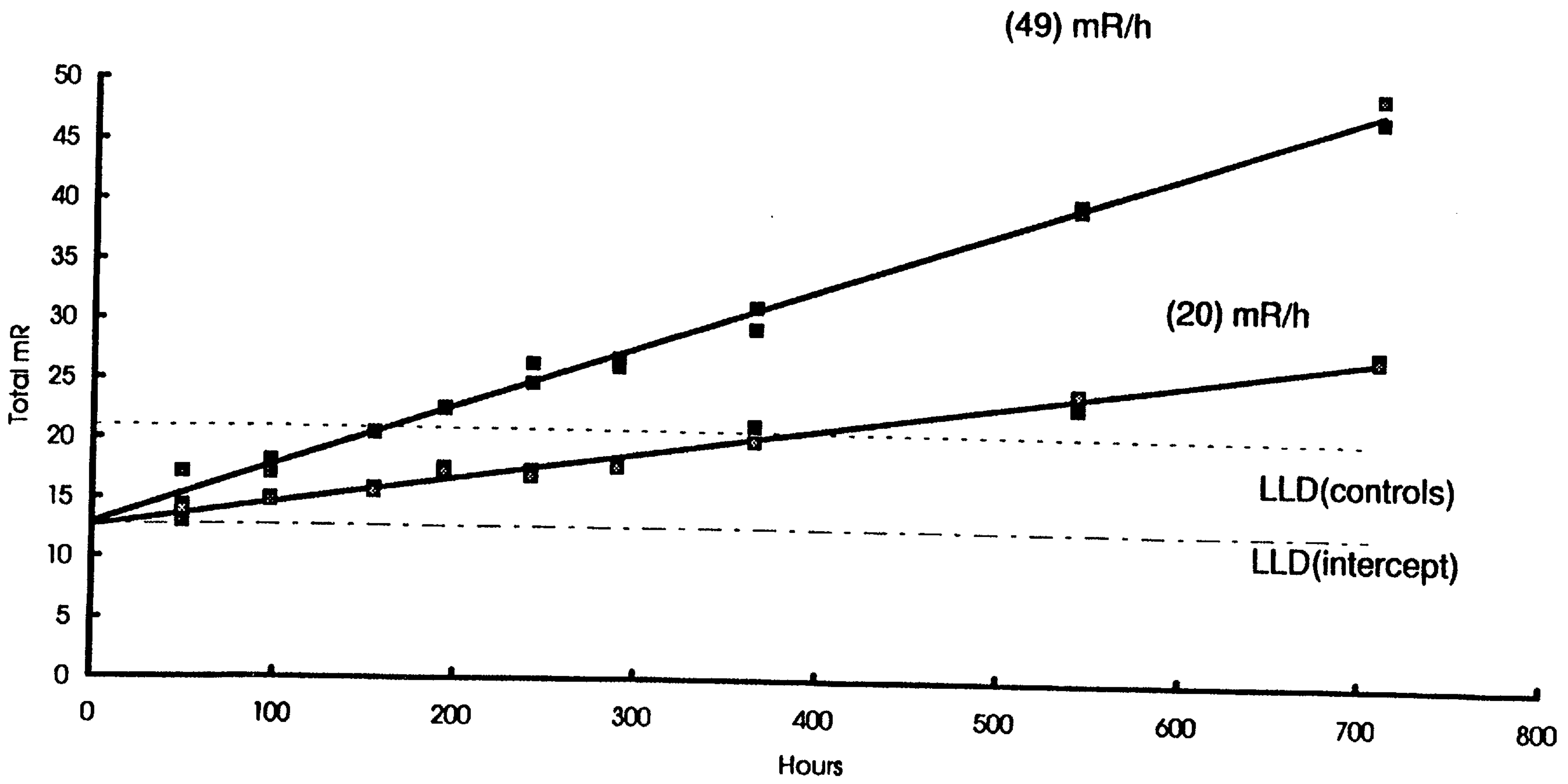

Figure 1. Measurements made with dosimeters at 2 dose rates to determine the detection limit (LLD). Two LLD's are shown, one based on the intercept and one based on the controls.

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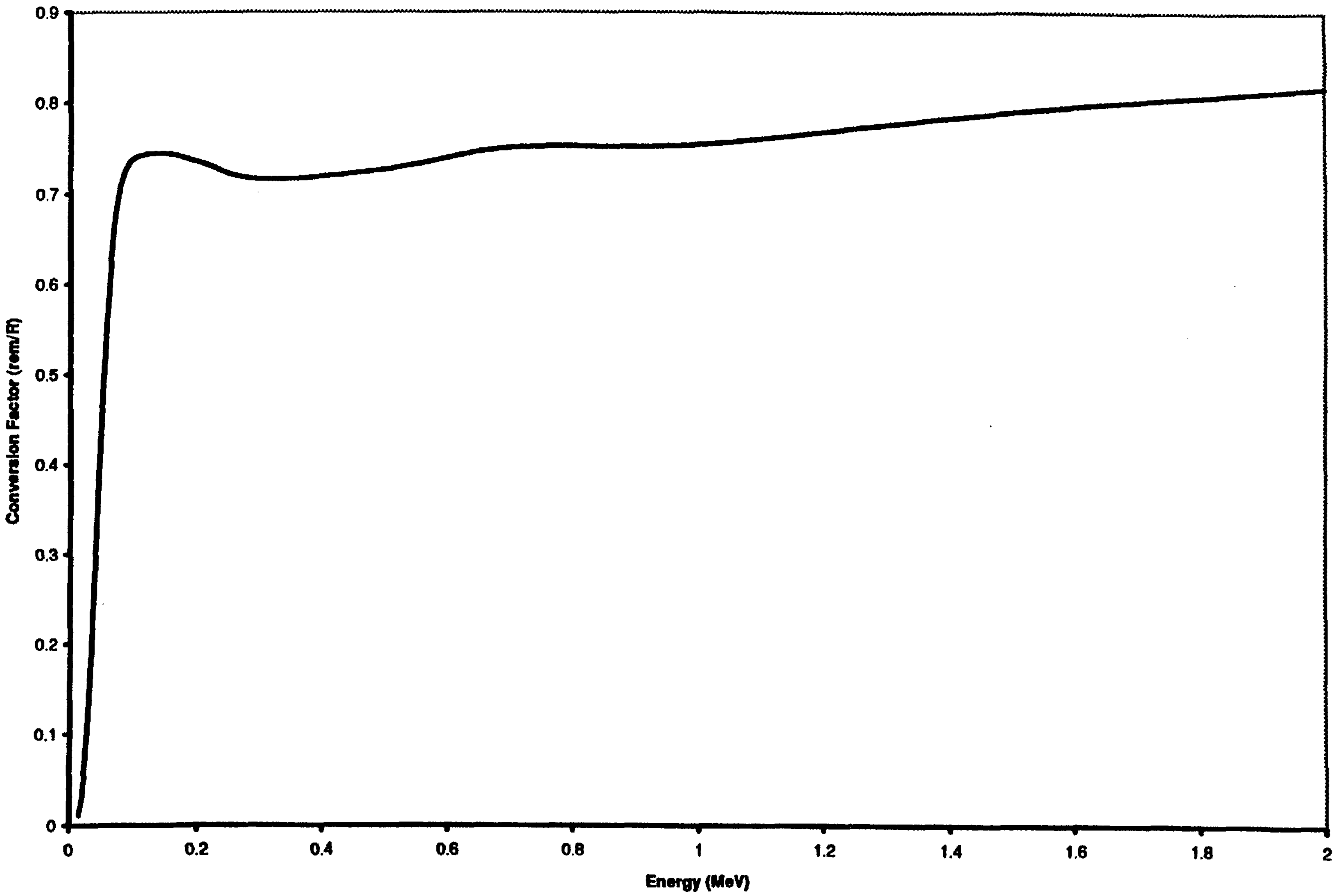

Figure 2. Energy dependent conversion for a body standing on an infinite plane source.

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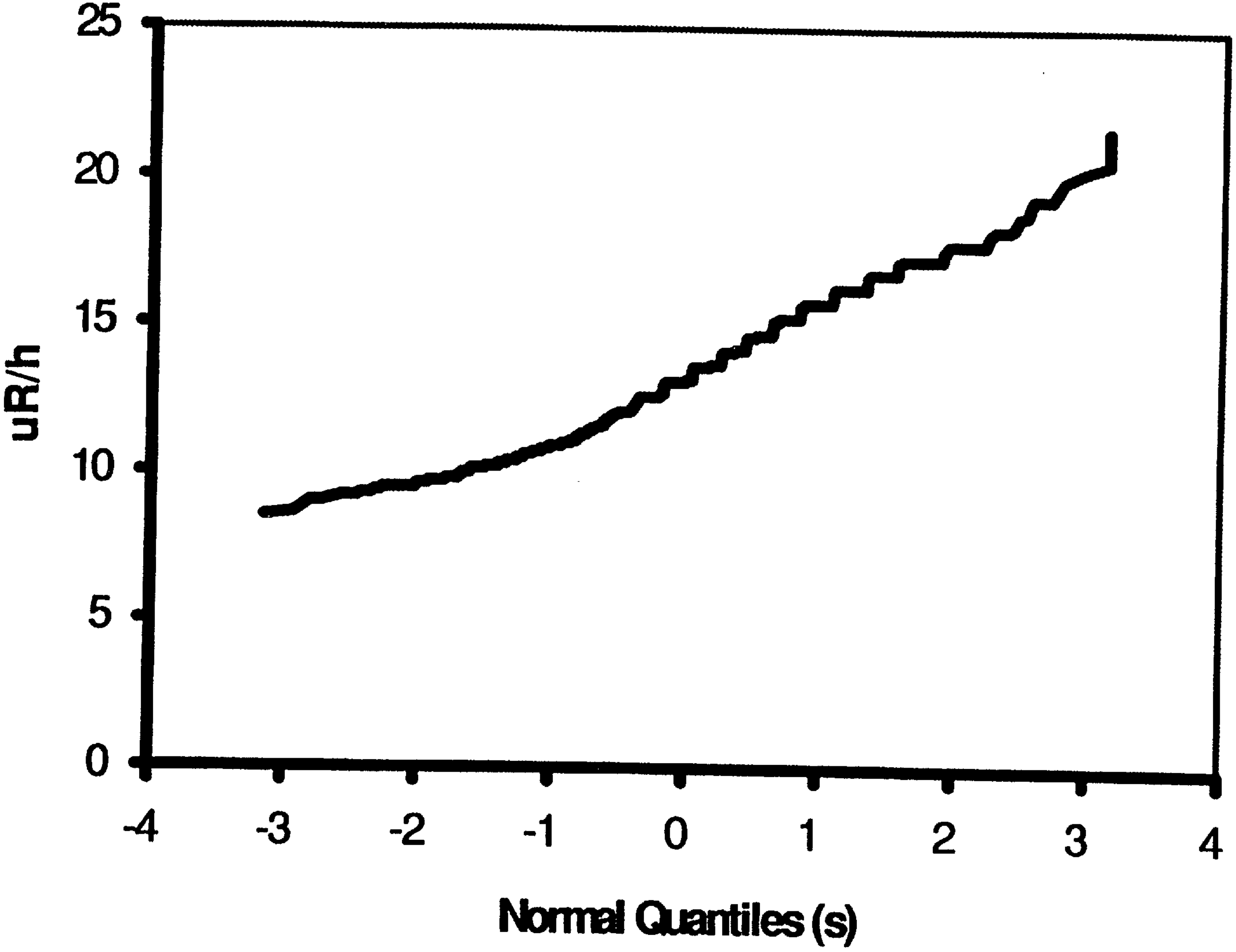

Figure 3. Probaility plot of background near a NORM site.

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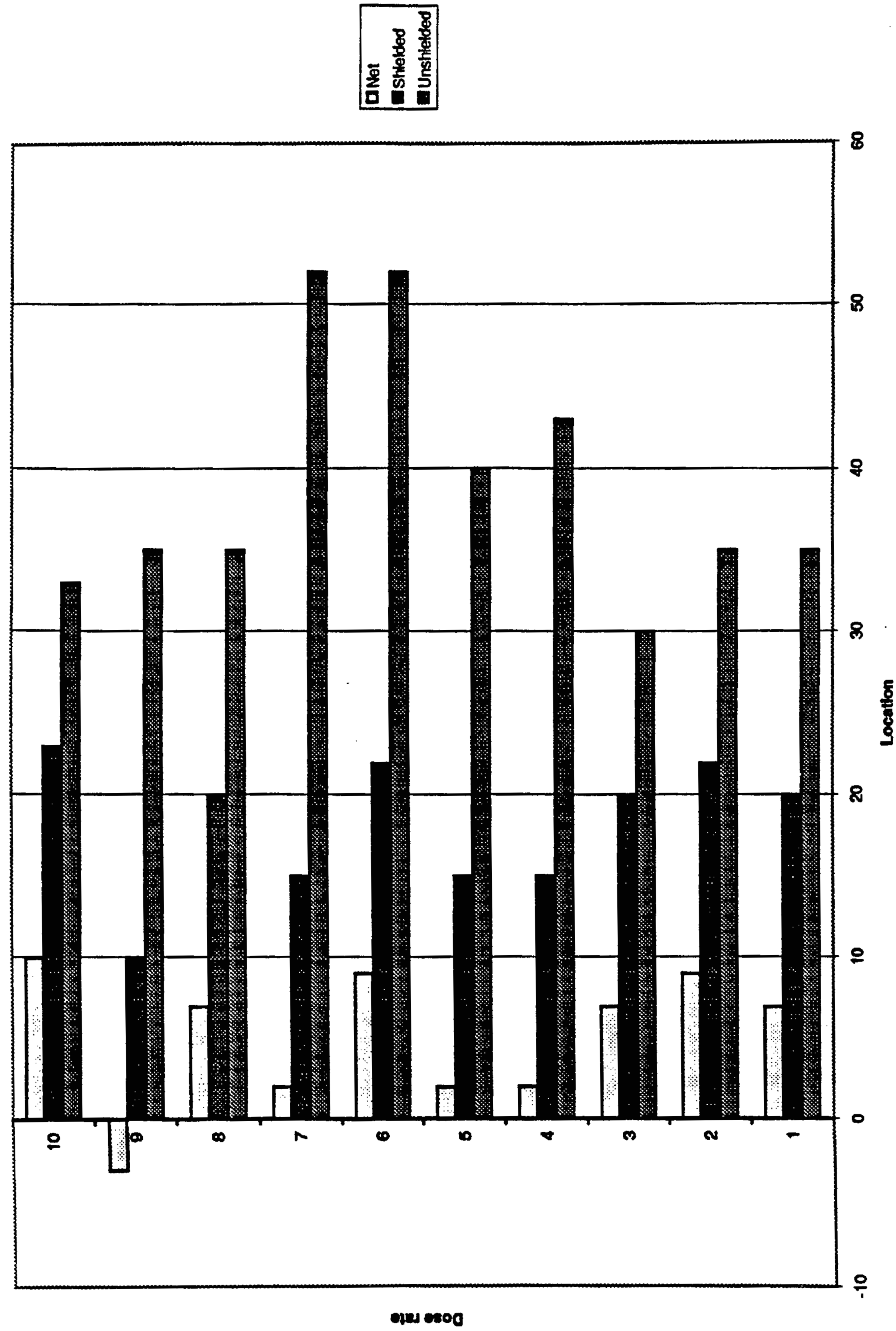

Figure 4. Dose rate measurements at several locations showing unshieled, shielded, net doses.

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EVALUATION OF NORM SITE RELEASE CRITERIA FOR UNRESTRICTED USE

Prepared for:
API GRI NORM Conference
Houston Texas.
October 16-18, 1995

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EVALUATION OF NORM SITE RELEASE CRITERIA

1.0 INTRODUCTION

NORM regulations contain differing criteria for use in the evaluation of remediated sites for release for unrestricted use. All regulations require sample collection and analysis to establish the radium 226 and 228 specific activity. The regulatory exempt level may be 5 or 30 picoCi/gram of radium 226 and/or 228 and may also include the requirement to measure(1) the radon emanation rate. This paper records the results of the site dose rate survey tabulated with the specific activity and radon emanation rates for a number of specific locations on a NORM contaminated site during and after remediation. One data set for radon emanation was collected before remediation and the others after clean up had been completed. In every case, the radon emanation rate was less than 2 picoCi/square meter/second regardless of the radium 226 and 228 concentration. The highest radon emanation rate of 1.8 $pCi/m^2/S$ was measured at a location where the radium 226 concentration was 113 pCi/gram. The extremely low radon emanation rates measured from this oilfield NORM remediation project strongly suggest that the use of radon emanation as a regulatory criteria for site release for unrestricted use could be discontinued and removed from NORM regulations applicable to oilfield NORM.

2.0 NORM REGULATIONS FOR SITE RELEASE FOR UNRESTRICTED USE

The project site clearance criteria following remediation was based on the following :

TABLE 1

TEXAS PART 46 NORM REGULATIONS SECTION 46.4 EXEMPTIONS

(i) (a) 30 picoCuries per gram or less of technologically enhanced radium 226 or radium 228 in soil, averaged over any 100 square meters and averaged over the first 15 centimeters of soil below the surface, provided the radon emanation rate is less than 20 picoCuries per meter squared per second,

(b) 30 picoCuries per gram or less of technologically enhanced radium 226 or radium 228 in media other than soil, provided the radon emanation rate is less than 20 picoCuries per square meter per second; or

(ii) (a) 5 picoCuries per gram or less of technologically enhanced radium 226 or radium 228 in soil, averaged over any 100 square meters and over the first 15 centimeters of soil below the surface, in which the radon emanation rate is 20 picoCuries per square meter per second.

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(b) 5 picoCuries per gram or less of technologically enhanced radium 226 or radium 228 in media other than soil, in which the radon emanation rate is 20 picoCuries per square meter per second.

3.0 SITE SURVEY SAMPLE COLLECTION ANALYSIS AND RELEASE CRITERIA DEVELOPMENT

Specific Activity

The entire site was surveyed using a ten (10) by ten (10) yard grid. All Hot Spots over twice background were identified and resurveyed using a three (3) by three (3) yard grid and where required some smaller areas were resurveyed using a one (1) by one (1) yard grid. The initial site background was measured at 4.5 to 5.2 microR/h and the criteria for Hot Spots at 9 to 10.5 microR/h.

Some sixty four samples were collected covering depth layers from 0 to 6, 6 to 12 and 12 to 18 inches over the full range of Hot Spot dose rates (10.5 to 1700) microR/h measured during the site survey. Eleven Hot Spot soil samples were selected covering the range of dose rates from a background of 6.0 microR/h to 800 microR/h and radiochemically analyzed to determine the depth of the contamination and evaluate the if there was a relationship between the dose rate and the site release criteria of 5 picoCuries /gram of radium 226 and 228.

TABLE 2

Summary Of The Location Dose Rate, Sample Dose Rate, and Specific Activity > 5 pCi/g

Location Dose Rate microR/h	Sample Dose Rate microR/h	Depth Inches	Specific Activity pCi/g Radium	
			226	**228**
800	4.4	0-6	686	169
24	8.2	0-6	8.8	6.5
14	4.6	0-6	5.2	0.8
8.2	4.6	0-6	9.0	1.5

OTHER READING WITH SPECIFIC ACTIVITY < 5 pCi/g

			226	**228**
40	3.7	6-12	1.1	0.5
20	160.0	0-6	2.6	0.9
18	5.8	0-6	3.6	1.1
12	5.0	12-18	1.7	0.5
12	4.8	12-18	3.4	0.7
11.5	4.6	0-6	3.0	1.5
7.2	5.2	0-6	0.9	<0.2

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Based on these results, the dose rate for site release purposes was raised from twice the local background of 10.5 up to the 14 micro/h level. Site remediation was initiated using this site screening dose rate with the objective of removing the minimum NORM contaminated material to leave the site with each composite sample having a concentration of less than 5 picoCuries/ gram of radium 226 or 228 to meet the exemption (ii) (a) above.

Examples of the Soil Sample Log showing the radiochemical summary results are shown in Appendix 1. The specific activities measured in these samples found that there was virtually no relationship between the dose rate and radium 226 or 228 concentrations. However, the site contamination was determined to be deeper than expected.

Radon Emanation Rate Measurement and Analysis

Measurement of radon 222 followed the Method 115 contained in 40 CFR Part 61, Appendix B and the EPA document 520/5-85-029, Radon Flux Measurements on Gardinier and Royster Phosphogypsum Piles Near Tampa and Mulberry Florida.

This method involves the sorbing of radon onto activated carbon granules mounted inside 10-inch diameter canisters. For the sample to be valid, the site must have been free of rain for twenty four hours and have no standing water. In addition, there must be no rain during the collection period.

Five sample caps each containing 180 grams of granulated activated carbon are evenly placed within a 100 square meter area and sealed to the ground using the local soil heaped up round the caps. They are left in place for twenty four hours to adsorb the radon and the time of collection, grid location and surface dose rate were recorded. Following collection of the five caps, the carbon was consolidated into one sample for radiochemical analysis. Soil samples from under each cap were collected and composited into one sample which was split with one split being sent for gamma spectrum analysis and the other archived.

This radon measurement method assumes that 100% of the radon is sorbed onto the carbon which is then analyzed for the bismuth 214 content at an energy level of 609 kev using a high resolution gamma spectrometer. The results of the dose rates, specific activities, and radon emanation rates for sixteen locations are illustrated in figure 1 and detailed in Appendix 2

QA/QC for Laboratory Analysis

Calibration for the radon flux measurements was done in accordance with the EPA procedures cited above. Radium 226 standards (from two different sources) were spiked into measured quantities of graphite granules, dried, transferred and sealed in Marinelli beakers and then allowed to sit for two weeks while the radon ingrowth occurred. These standards were then used to determine the efficiency of the germanium detector (about 1% efficient) based on the geometry of the system. In addition to using traceable standards from different sources, blank samples of the activated charcoal granules were taken each time to ensure the activated carbon did not sorb radon from errant sources. The spread sheet algorithm used to calculate the radon emanation rate was checked using raw data from the EPA.

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Quality control protocols for the radium 226 and radium 228 measurements are routine and rigorous. Blanks, standards (from multiple sources) were used to calibrate and monitor the performance of the system. Energy calibrations are performed on a daily basis and efficiency calibrations are performed on a periodic basis to check the accuracy of the analytical system. Reference standards were also analyzed on a periodic basis to ensure that the results are within the statistical uncertainty established for the project.

4.0 NORM SAMPLING METHODOLOGY

All areas defined as hot sots were excavated and then field screened for dose rate levels (microR/h) and sampled for specific activity (picoCuries /gram).The material screened and determined to contain low dose rate levels were also sampled for specific activity. Selected excavated areas were sampled for radon flux ($pCi/m^2/s$). Specific activity levels and radon flux were sampled using the following methodology.

Soil Samples

Nine sixteen ounce samples were taken from each 100 square yards and composited into one bulk sample of 144 ounces. Two 16 ounce samples of soil were then taken from this composite. One was archived and the other sent for radiochemical analysis for specific activity. Some 3200 samples were collected and composited into 355 samples which formed the sample population.

NOTE: Not all samples collected were sent for laboratory analysis. A sub sample, of the total sample population was selected using a random number generator, with a sufficient sample size selected to statistically represent the sample set to within 2 standard deviations of the sample mean and a maximum error allowed to be 0.25 pCi/g of radium 226.

Radon Samples

Sixteen radon samples were taken at excavated areas throughout the yard to represent the radon flux. Five ten inch diameter heavy plastic caps each containing 180 grams of charcoal were evenly placed within a 10 yard by 10 yard square. The charcoal was allowed to adsorb the radon for twenty four hours with the times carefully recorded. The five 180 gram samples were then composited into one 900 gram sample and sent to the laboratory for analysis. The sampling condition requiring dry weather for twenty four hours prior to collection and during the collection period limited the number of samples taken during this project. To check for the possible adsorption of radon onto the plastic caps and the possible reduction in the measured radon emanation rate two additional sets of caps were made up from aluminum pie dishes. The matching radon measurements from the same location are samples 15 (Plastic) and 16 (Metal) for the first location 17 (plastic) and 18 (Metal) from the second location in Appendix 2 and Figure 1. The radon emanation rates were all low and in general agreement with previous studies.(2)

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5.0 SAMPLE ANALYSIS RESULTS, CONCLUSION, AND RECOMMENDATIONS

The sample locations, dose rate, soil specific activity and radon flux results are given in Appendix 2 and shown in Figure 1. For NORM concentrations of 30 pCi/gram of radium 226 spread over one square meter and 15 centimeters depth assuming 100% collection of all radon 222 on the granulated carbon then the calculated maximum emanation rate will be 14 $pCi/m^2/S^{(3)}$.

Soil Samples Conclusions

1. The soil samples analyzed confirmed that the site had been remediated to the 5 pCi/g radium 226 and 228 level set for the project.

2. Soil samples measuring over the target release level were recleaned to meet the 5 pCi/g radium 226 limit for the project..

Radon Samples Conclusions

1. All radon samples were less than 2 $pCi/m^2/S$.

2. For NORM on this site with a radium 226 concentration of 113 pCi/g the measured radon emanation rate was 1.8 $pCi/m^2/S$.

3. The plastic caps gave higher radon emanation rates than the metal caps hence it appears that from the results of this study they do not adsorb the radon and that their use for holding the activated charcoal is acceptable.

4. There is a need for more radon sampling in association with oilfield NORM site remediation to further document the usefulness of radon emanation rate measurement as a regulatory criteria for site release for unrestricted use.

Recommendations

1. NORM site remediation projects should continue to collect radon emanation data to expand the developing data base contained in this paper.

2. The use of radon emanation rates as a regulatory criteria for oilfield NORM site release for unrestricted use should be reviewed and based on the results of this paper removed from the NORM regulations.

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References:-

1 Method 115 40 CFR Part 61 Document 520/5-85-029 Radon Flux Measurement on Gardinier and Royster Phosphogypsum Piles near Tampa and Mulberry, Florida.

2 Radialogical Characterization of the Martha , Kentucky, Remediated Tank Battery Sites. by Scott L. M. Herbert M.B. 1993

3 NORM Disposal Advisory Group paper discussing Radon 222 Emanation Rates. by Dr Irwin R. Supernaw Texaco.

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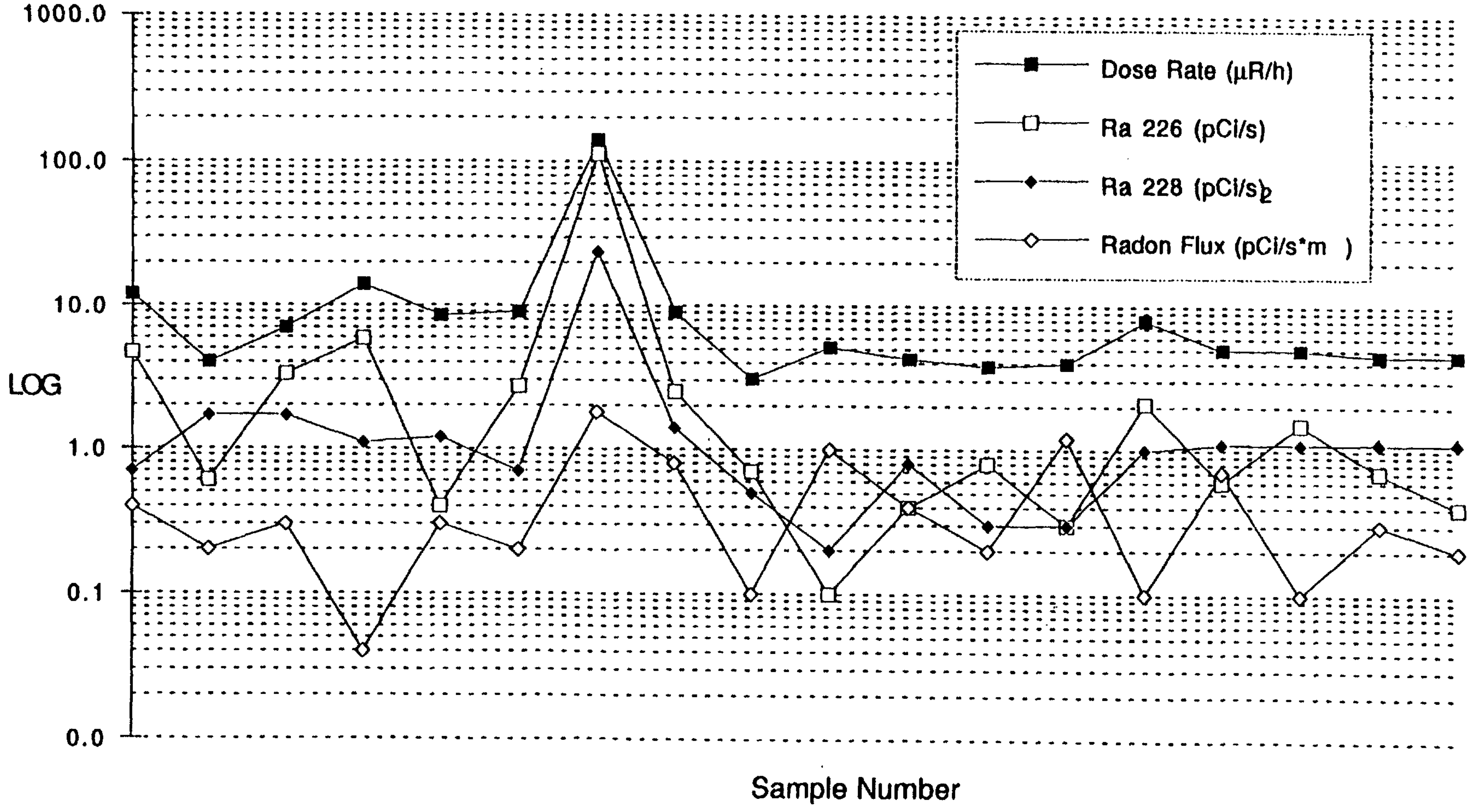
FIGURE 1

DOSE RATE-SPECIFIC ACTIVITY-RADON EMANATION RELATIONSHIP



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APPENDIX 1
NORM SITE SURVEY
SOIL SAMPLE LOG

Location on Grid	Sample Dose Rate µR/h	Location Dose Rate µR/h	Depth (0-6", 6-12", etc.)	Specific Activity Ra 226 (pCi/s)	Specific Activity Ra 228 (pCi/s)
Not Used		nt			
Not Used		nt			
AE49-50	1700.0	550.0	0"-2"		
AE49-50	1700.0	150.0	2"-4"		
AE49-50	1700.0	68.0	4"-6"		
AE49-50	1700.0	12.0	6"-12"		
AE49-50	1700.0	9.2	12"-18"		
AE49-50	1700.0	500.0	Bedlayer 2" TO 3" Thick		
AH53	26.0	16.0	Hill West 0" to 6"		
AH53	26.0	9.2	Hill West 6" to 12"		
AH53	26.0	7.6	Hill West 12" to 18"		
AH53	90.0	14.0	Hill West 0" to 6"		
AH53	90.0	6.6	Hill West 6" to 12"		
AH53	90.0	7.5	Hill West 12" to 18"		
Pipe Rack	60.0	6.6	Hill West 0" to 2"		
15' North of Building	60.0	7.6	Hill West 2" to 4"		
5' West from Pipe Rack	60.0	24.0	Hill West 4" to 6"		
Pipe Rack West	60.0	9.2	Hill West 6" to 12"		
South East corner of Bldg.	880.0	260.0	Hill West 0" to 6"		
South East corner of Bldg.	880.0	21.0	Hill West 6" to 12"		
South East corner of Bldg.	880.0	7.2	Hill West 12" to 18"		
North Side Bldg.	400.0	14.0	Hill West 0" to 2"		
North Side Bldg.	400.0	30.0	Hill West 2" to 4"		
North Side Bldg.	400.0	54.0	Hill West 4" to 6"		
North Side Bldg.	400.0	6.8	Hill West 6" to 12"		
HB Building	160.0	7.8	Hill West 0" to 2"		
HB Building	160.0	9.2	Hill West 2" to 4"		
HB Building	160.0	300.0	Hill West 4" to 6"		
HB Building	160.0	200.0	Hill West 6" to 12"		
HB Building	160.0	9.4	Hill West 12" to 18"		

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APPENDIX 1
NORM SITE SURVEY
SOIL SAMPLE LOG

Location on Grid	Sample Dose Rate µR/h	Location Dose Rate µR/h	Depth in inches	Specific Activity Ra 226 (pCi/s)	Specific Activity Ra 228 (pCi/s)
0-18/0-19	40.0	4.2	6		
0-18/0-19	40.0	3.7	12	1.1	0.5
0-51/E-51	800.0	4.4	6	686.0	169.0
0-51/E-51	800.0	5.2	12		
0-51/E-51	800.0	5.0	18		
E-11/E-10	18.0	5.8	6	3.6	1.1
E-11/E-10	18.0	4.2	12		
N-24/N-25	20.0	160.0	6	2.6	0.9
N-24/N-25	20.0	85.0	12		
L-31/L-30	24.0	8.2	6	8.8	6.5
L-31/L-30	24.0	4.7	12		
L-31/L-30	24.0	4.5	18		
E-3/F-3	11.5	4.6	6	3.0	1.5
E-3/F-3	11.5	4.4	12		
L-23/L-24	8.2	4.6	6	9.0	1.5
L-23/L-24	8.2	4.8	12		
B-38/C-38	14.0	4.5	6	5.2	0.8
B-38/C-38	14.0	4.8	12		
Y-11/Z-11	12.0	4.6	6		
Y-11/Z-11	12.0	4.8	12		
Y-11/Z-11	12.0	5.0	18	1.7	0.5
V-11	6.0	5.0	6		
PIT	7.2	5.2	6	0.9	<0.2
Y-12/Z-12	12.0	4.2	6		
Y-12/Z-12	12.0	4.5	12		
Y-12/Z-12	12.0	4.8	18	3.4	0.7
Not Used					
Not Used					
Not Used					
Not Used					
Not Used					
Not Used					
Not Used					
Not Used					

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APPENDIX 2
SAMPLE RESULTS LOCATION, DOSE RATE, SPECIFIC ACTIVITY, AND RADON EMANATION

Sample No.	Date Sampled	Associated Grid Location	max µR/h at surface	max µR/h at 15 cm depth	Soil Type*	Specific Activity Ra 226 (pCi/s)	Specific Activity Ra 228 (pCi/s)	Associated Radon Sample No.	Radon Flux (pCi/s*m*m)
76	11-Aug-95	H59	12.0	nt	GP	4.7	<0.7	1	0.4±0.035
77	11-Aug-95	Background	4.0	nt	GP	<0.6	1.7	2	0.2±0.026
123	16-Aug-95	AF50	7.0	10.0	SW	3.3	1.7	3	0.3±0.024
124	16-Aug-95	K12	14.0	27.0	ML	5.9	<1.1	4	0.04±0.028
125	17-Aug-95	D51	8.5	15.0	GW-ML	<0.4	<1.2	5	0.3±0.031
126	17-Aug-95	V31	9.0	10.0	GP	2.7	<0.7	6	0.2±0.024
127	18-Aug-95	AG50	140.0	200.0	SP	113.0	23.7	7	1.8±0.071
128	18-Aug-95	V31	9.0	9.5	SP	2.5	1.4	8	0.8±0.049
132	25-Aug-95	D2	3.1	3.2	SP	<0.7	<0.5	9	0.1±0.016
133	25-Aug-95	Z12	5.2	5.8	SP	<0.1	<0.2	10	<1.0±0.016
179	3-Sep-95	N40	4.3	3.8	SP	<0.4	<0.8	11	0.4±0.031
180	3-Sep-95	L16	3.8	3.2	SP	<0.8	<0.3	12	0.2±0.024
181	3-Sep-95	S49	4.0	4.1	SP	<0.3	<0.3	13	1.2±0.045
182	3-Sep-95	L51	8.0	8.5	SP	2.1	1.0	14	0.1±0.013
360	9-Jan-04	ROCKPILE	5.0	5.1	SP	<0.6	<1.1	15	0.7±0.04
361	9-Jan-04	ROCKPILE	5.0	5.6	SP	<1.5	<1.1	16	0.1±0.01
362	9-Jan-04	STOCKPILE	4.5	5.2	SP	<0.7	<1.1	17	0.3±0.03
363	9-Jan-04	STOCKPILE	4.5	5.5	SP	<0.4	<1.1	18	0.2±0.02

GP = POORLY-GRADED GRAVEL
SW = WELL-GRADED SAND
SP = POORLY-GRADED SAND
ML = INORGANIC SILTS AND VERY FINE SANDS

* USING ASTM D2488, Standard Practice for Description and Identification of Soils

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RADIOACTIVE LEAD: AN UNDERESTIMATED NORM ISSUE?

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SUMMARY

The encounter of Naturally Occurring Radioactive Material (NORM) is of increasing concern for the oil and gas industry, not only because of radiological safety aspects, but also from an environmental point of view. Attention with respect to NORM in the E&P industry has been focused mainly on radium and its progeny, as encountered in scales and in sludges. With the commonly used measuring tools, a from a radiological safety point of view important nuclide: ^{210}Pb can easily be overlooked. ^{210}Pb in oil and gas producing or treating facilities may originate from three different transport mechanisms: as a daughter of ^{226}Ra, transported with the aqueous phase; as a daughter of ^{222}Rn, transported in the gas phase or as 'unsupported' ^{210}Pb, which is, as shown by stable isotope analysis, carried from the subsurface to the facilities with (stable) lead isotopes from the brine/ground water in the gas phase or together with hydrocarbon condensate. This 'unsupported' ^{210}Pb, with specific activities of about 1,000 Bq/g, can be incorporated in massive metallic (lead) lumps or in specific lead compounds, such as laurionite.

INTRODUCTION

The presence of radioactive materials in the non-nuclear industry, when originating from the primordial decay series of ^{238}U, ^{235}U or ^{232}Th, frequently abbreviated by the acronym NORM (Naturally Occurring Radioactive Materials), is generally established by the observation of (penetrating) γ-radiation. The main γ-emitting daughter nuclides from the ^{238}U, ^{235}U or ^{232}Th series are respectively ^{214}Bi and ^{214}Pb; ^{223}Ra and ^{228}Ac, ^{212} Pb and ^{208}Tl. Due to the low natural abundance of ^{235}U (0.28%), members of this series are only occasionally encountered in E&P NORM.

The attention of the oil and gas producing and treating industry with respect to the presence of NORM has been focused mainly on radium containing carbonate-, sulphate- or silicate-scales in equipment and in solid and liquid waste streams. A schematic outline of a production train, showing the places where NORM contaminants are commonly encountered, is given in Figure 1.

It is common, that the absence of (external) γ-radiation, in combination with the absence of ^{222}Rn, is used as an indication for the absence of NOR's (Naturally Occurring Radionuclides) in products, by-products, waste streams and installations or equipment.

Particularly in natural gas production and treating industries however, two important (both from a radiation protection point of view as well as from environmental considerations) might then be overlooked: the isotope ^{210}Pb emitting low energy γ-photons and its α-emitting daughter nuclide ^{210}Po. Both radionuclides have been observed to occur as unsupported[a] nuclides (*i.e.*, without their ancestors) in natural gas products and in treating installations and these nuclides may, when unnoticed, impose a serious health threat.

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[a] For terminology see W.A.I. Knaepen, W. Bergwerf and G. Jonkers, Determination of Naturally Occurring Radionuclides in Samples from the Gas and Oil Industry, this conference proceedings, (ref. 23).

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Whereas it is generally agreed, that the radium isotopes are transported with the brine phase (formation or production water) and that unsupported radon is transported from the reservoir to the surface with the gas phase, in the literature thus far little or no references have been found regarding occurrence and transport mechanism of unsupported lead or polonium.

NATURAL DECAY SERIES in the OIL and GAS INDUSTRY

The nuclides from the natural decay series in 'closed' systems (*i.e.* under conditions where radionuclides are not transported away from their site of deposition and remain present, undisturbed by leaching or evaporation/emanation processes for long periods of time compared to the half-live of the parent nuclide) are present in activity (but NOT mass) concentrations equal to the activity concentration (in Bq/g) of the parent nuclide. Under these secular equilibrium conditions[b], the activity concentration of the radionuclides decreases with the half-life of the parent isotopes ^{238}U or ^{232}Th. The decay of the individual daughter nuclides is compensated (or supported) by the continuous supply from its parent nuclide.

In 'open' systems, where evaporation or leaching processes can remove radionuclides at different rates, no secular equilibrium exists. In reducing environments, as found in oil and gas fields, uranium and thorium are present in immobile chemical forms, whereas radium can easily be transported with chloride rich brines. Once *e.g.* radium isotopes are leached from their lithological origin, they are no longer supported by their ancestors and may, under closed system conditions develop their 'own' decay sub-series.

In the oil and gas industry, the 'complete' ^{238}U or ^{232}Th decay series has only been observed in reservoir material (like cuttings or sand fractions) and in streams, which contain these materials (*e.g.* in drilling mud and certain sludge fractions). The concentrations of ^{238}U or ^{232}Th and their progeny in the particulates from these fractions is within the same range as found in the corresponding reservoir material.

The four sub-series which constitute the NORM in the oil and gas industry, are shown in Figures 2 and 3. 'Parent' nuclides in E&P NORM are:

- ^{228}Ra (be it in secular equilibrium with ^{224}Ra and its short lived daughters or not);
- ^{226}Ra, in secular equilibrium with its progeny up to ^{210}Pb;
- ^{222}Rn, in secular equilibrium with its progeny up to ^{210}Pb and, as described in this paper,
- ^{210}Pb, in secular equilibrium with ^{210}Po;
- ^{210}Po, as an unsupported radionuclide.

LEAD-210 IN NORM

As indicated in the previous section, ^{210}Pb in equipment, products, by-products and waste streams from the oil and gas producing and treating industry can have different origins.

Lead, Supported by Radium and its Detection

Many observations of NORM in E&P operations have confirmed the presence of ^{226}Ra, ^{228}Ra and ^{224}Ra and their progeny in scales, sludges, deposits and (aqueous) waste streams. It is noteworthy that enhanced concentrations of either ^{238}U or ^{232}Th (parents of the main natural decay series) and their

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[b] The rate at which secular equilibrium between a radioactive 'mother' and its also radioactive 'daughter' is established, is determined by the decay constant of the daughter nuclide. Secular equilibrium between ^{226}Ra and e.g. ^{222}Rn is reached for more than 95% after 5 half life times of ^{222}Rn (19 days), whereas the same degree of build-up of ^{210}Pb from ^{226}Ra, in 'closed' systems from which none of the intermediate radionuclides can escape, is only reached after 110 years.

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daughters up to the radium isotopes have not been detected in NORM products from oil and gas exploration and production.

It is generally believed that this borderline, which separates the radium isotopes from their ancestry, originates from the specific geochemical properties of radium (*i.e.*, mobility under reservoir conditions). The driving force for the transport of radium from the reservoir to (sub)surface structures appears to be the (forced) movement of production water. Radium containing NORM products generally are observed at installation parts and in waste product streams where also calcium, barium or strontium deposits are found and in which radium is co-precipitated in silicates, in sulphate or in carbonate salts. Since ^{226}Ra is the parent of ^{222}Rn, which in its turn decays into ^{210}Pb which ultimately forms ^{210}Po, in radium containing scales generally all isotopes from the ^{238}U or ^{232}Th decay series below the radium isotopes are also present, whether in secular equilibrium with each other or not. ^{226}Ra supported ^{210}Pb activity concentrations of up to 1,000 Bq/g have been reported.

The presence of this type of NORM contamination in E&P installations can generally be established by an external (γ-)radiation survey. Especially the ^{226}Ra daughter ^{214}Bi, the ^{228}Ra daughter ^{228}Ac and the ^{224}Ra daughter ^{208}Tl are "hard" γ-emitters, which easily penetrate the steel walls of vessels and tubing. Whether installations are in production or not, the external γ-radiation from the short-lived radium daughters only decreases with the half-life of the parent radium isotopes.

Lead, Supported by Radon and its Detection

A second, less known, form of NORM can be found specifically in natural gas treating installation parts, *i.c.*, in fractionators and in NGL storage tanks. The noble gas ^{222}Rn, with a boiling point of -61.8 °C, has such a partitioning coefficient that it tends to be concentrated in the liquid phase. Especially in C_2 and C_3 fractionators concentration factors of more than 1,000 have been observed. Upon decay of ^{222}Rn very thin (almost invisible) layers of ^{210}Pb can be formed at the inner surface of gas transport lines, treating- or storage installations, with activity concentrations up to 1,000 Bq/g. This isotope is the grandparent of the radiotoxic α-emitter ^{210}Po; inhalation or ingestion of ^{210}Pb/^{210}Po, during inspection or maintenance, might easily lead to effective doses in excess of the recommended ICRP dose limits.

Especially in installation parts where the mean residence time of ^{222}Rn is long enough to allow a (significant) fraction to decay and where, by enrichment, its concentration is increased, very thin ^{210}Pb deposits might be formed. The presence of these deposits can be established externally from the increased γ-radiation levels from the short-lived ^{210}Pb ancestor ^{214}Bi; this radiation quickly disappears once the supply from ^{222}Rn is stopped (*e.g.* when the vessel is vented). The radioactive lead deposits remain present; the γ-radiation from ^{210}Pb however is too weak to be measured externally (E_γ = 47 keV, 4%; $E_{\beta\,(max)}$ = 61 keV; half-life 22 years).

The observation of external γ-radiation from NORM surveys during operations, will provide adequate warning signals to the radiation safety adviser for the presence of ^{210}Pb/^{210}Po. The implementation of adequate Standard Operation Procedures for inspection or maintenance activities will be sufficient to prevent unintended exposure of the workforce.

Unsupported Lead

Recently, it has been observed that ^{210}Pb can also be present in gas processing/treating facilities as an unsupported radionuclide, *i.e.*, in amounts which are much higher than can be explained from the ^{222}Rn concentrations in the gas which is treated or processed in the facilities[c]. The external "warning" radiation from ^{214}Bi which can be detected in NGL processing units, is lacking and unintentional exposure might easily take place.

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[c] Both unsupported ^{210}Pb and unsupported ^{210}Po has been observed in hydrocarbon condensates co-produced with natural gas (cf. also ref. 23).

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This type of unsupported $^{210}Pb/^{210}Po$ has been observed in two morphologies:

- as yet unidentified chemical forms in hydrocarbon condensate and in sludges, but also in scrapings from clean (to the naked eye) tubing and even on spheres used for pipe cleaning purposes ("pigs") with activity concentrations in the order of 10 $Bq[^{210}Pb]/g$ and
- as part of massive "metallic" lumps (sizes of up to several centimetres), consisting of either elemental lead or distinct lead compounds[d], such as laurionite ($Pb[OH]Cl$) with activity concentrations of circa 1,000 $Bq[^{210}Pb]/g$.

"On site" detection of unsupported $^{210}Pb/^{210}Po$, with rigid explosion proof monitors, is unfortunately not possible. In the case of the nearly invisible films, the weak γ-radiation is readily absorbed by the steel walls. Even in the case of films with relatively high surface activity, external radiation detection is not possible, because of the lack of mass (thus of total activity in the field of view of the monitor). In the case of massive lumps, self-absorbtion of the γ-radiation will very much obscure the picture. The use of very sensitive γ- or β-radiation monitors generally is prohibited at E&P treating and production sites because of safety reasons.

ORIGIN OF 'UNSUPPORTED' LEAD COMPOUNDS

Whereas the origin of ^{210}Pb in radium containing scales is presumably the transport *via* the brine phase and ^{210}Pb in NGL installations is formed as a decay product from the gas phase, the transport mechanism and the origin of unsupported lead are not well understood. In order to get a better understanding of unsupported lead in these deposits, lead stable isotope analysis have been carried out.

Lead stable isotope composition

Four stable lead isotopes are found in nature: ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb[1]. The last three isotopes are commonly denoted as "radiogenic lead", since they are the (stable) end members of the ^{238}U, ^{235}U and ^{232}Th decay series. ^{204}Pb, which has not been formed from a naturally occurring radioactive parent nuclide, is considered non-radiogenic.

Table 1: **Stable lead isotope composition (% m/m) of "lead" and "laurionite" samples.**

Sample	^{204}Pb (non-radiogenic)	^{206}Pb (^{238}U series)	^{207}Pb (^{235}U series)	^{208}Pb (^{232}Th series)
NBS-981	1.4255	24.1442	22.0883	52.3470
"Laurionite"	1.339	25.137	21.018	52.369
Relative Enrichment	-6.05%	+4.11%	-4.85%	+0.04%
"Lead"	1.352	25.268	21.185	52.196
Relative Enrichment	-5.16%	+4.65%	-4.09%	-0.31%

The isotopic composition of any lead containing sample (liquid or solid, rock, mineral, sand or deposit) may be modified both by decay of U and Th present in the sample, as well as by the mixing with Pb having different isotope compositions. As a result, the isotopic compositions of Pb in rocks and ore

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[d] The identity of these compounds has been determined by elemental analyses techniques, in combination with X-ray diffraction and IR spectroscopy. In the paragraphs below, these two specific samples shall be denoted as "lead" and "laurionite".

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deposits display complex patterns of variation that reflect their geologic histories.

Both 'unsupported lead' samples ("lead" and "laurionite") are (significantly) enriched in radiogenic lead (^{206}Pb) from the ^{238}U series, whereas no enrichment in ^{208}Pb (from the ^{232}Th series) is observed. These results (see Table 1) are in agreement with the radiochemical analysis, where also only ^{238}U progeny is detected.

Geological age and origin of "lead" and "laurionite" samples

The isotope ratios ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb in minerals are indicative for the geological origin of the deposit[2] and they also can be used to calculate its age[3]. Comparison with published isotope ratios[4] indicate that both samples are deposits of *very* recent origin (0 Ga, within the accuracy of the applied model).

When the isotope ratios of these samples are compared with published data of lead minerals[5,6,7] and with those of (recent) oil field brines[8,9], a remarkable similarity between the isotopic composition of these samples and oil field brines from Mississippi, Texas, Alabama and the Cheleken Peninsula and with the specified average crustal lead isotope ratios[10] is observed. This is shown in Table 2, where the relative variations in lead stable isotope composition are, in analogy with the conventions for oxygen, carbon and hydrogen stable isotope abundances, expressed as:

$$\delta^{20x}\mathrm{Pb}(o/oo) = [\{(^{20x}\mathrm{Pb}/^{204}\mathrm{Pb})_{sample} - (^{20x}\mathrm{Pb}/^{204}\mathrm{Pb})_{standard}\}/(^{20x}\mathrm{Pb}/^{204}\mathrm{Pb})_{standard}] \times 1000,$$

where 20x = 206, 207 or 208 and the lead isotope ratios from NBS - 981 are used as standard.

Table 2: **Stable isotope ratios of some common minerals, oil field brines and oil field lead deposits.**

Ref.	Description	δ^{206}Pb(o/oo)	δ^{207}Pb(o/oo)	δ^{208}Pb(o/oo)
	Laurionite sample	108.4	13.3	65.0
	Lead sample	103.6	11.6	51.4
2	Galena (various sources)	-2.8 - -194.7	-8.5 - -44.0	-38.2 - -70.3
2, 6	Galena (radiogenic lead)	142.3 - 316.6	12.2 - 60.0	75.1 - 102.9
10	Average earth crust	104.1	8.8	52.0
7	Oil field brines (Mississippi)	90.4 - 108.8	7.2 - 11.1	49.9 - 55.2
8	Oil field brines & scales (Texas)	115.0	9.7	57.5
9, 11	Oil field brines & scales (Cheleken)	112.6	17.9	62.4
8	Salton sea oil field scales	128.4 - 134.8	9.0 - 18.7	61.2 - 72.7
8	Red Sea brine scales	105.3	12.2	49.0

Lead in oil- and gas field deposits

The presence of (non-radioactive) lead in oil- and gas field deposits has been mentioned in the literature. Several papers deal with a phenomenological description, whereas few publications suggest possible mechanisms.

From the brines of the Mississippi Raleigh oil field metallic lead and zinc deposits have been formed. The lead isotope ratios of these deposits are similar to those of the brines from the same oil fields; ^{210}Pb specific activities have not been determined, neither is the occurrence of radioactive isotopes in the deposits mentioned. The amount of base metals produced for the entire Raleigh field - Mississippi (two

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square miles) between 1966 and 1971 can be estimated at 85 tons of lead and 372 tons of zinc[15]. Similar observations have been described by Lebedev[11].

It is generally agreed that basinal brines, and oil-field brines in particular, are favoured ore-forming solutions[12]. Oil field brines are responsible for the formation of the rich lead - zinc deposits in the central Mississippi Salt Dome basin[13]. Macqueen and Powell[14] indicated that the geological development of a lead - zinc deposit is closely associated with the process of petroleum generation from organic matter in the surrounding regions. It has been suggested that a genetic relation (and thus a significant transport of sulphur and - presumably - metals) exists between the sulphur isotopes in the organic matter and the lead - zinc sulphate. Also mercury (and zinc) deposits appear to be of the same origin as the petroleum in a California cinnabar deposit[15]. High mercury concentrations have been detected in the crude oils and associated gases from wells near this mercury rich deposit (up to 20 ppm), which indicates the existence of a significant mercury transport from the cinnabar to the oil and gas phase, but the mechanism of this transport is yet unclear.

Tunn[16] reported an average concentration of 1 $\mu g/m^3$ (STP) lead in natural gases from Germany; lead concentrations in reservoir rock varied from 0.2 - 54.0 ppm. He supposed that relatively volatile heavy metals (such as mercury, lead, thallium, bismuth and cadmium) or their (organometallic) compounds or co-ordination complexes diffuse from the rock matrix into the reservoir gases. This process can be stimulated by pressure decreases in the reservoir, as caused by *e.g.* production from the reservoir.

Formation of "laurionite"

Laurionite is stable at (subsurface) conditions; it decomposes (at 1 atm) at its melting point of 415 K into $PbCl_2.PbO$ and water; At higher pressures, decomposition is observed at 490 K or above[17]. In the literature, several routes to natural laurionite have been published:

- it can be formed by the reduction of galena (PbS) under hydrothermal conditions[18]. Metallic lead, which is supposed to be an intermediate in this reaction, reacts with chloride ions in a basic (aqueous) environment.
- it has also been reported[19] as a lead corrosion product, deposited on buried lead pipes and on Roman artefacts, found in the Mediterranean. The proposed mechanism requires an oxidizing environment.
- the partial hydrolysis of chloride complexes of lead, has also been found to produce laurionite; precipitates with amongst others this compound were identified on the casings of boreholes in the Cheleken anticline[20].
- In a recent study on the formation of lead minerals Edwards *et al.*[21] showed that: *under natural saline conditions, seawater for example, where approximate chloride concentrations are 0.5 M, and the pH is about 8, the preferred phase to crystallise would be laurionite or its dimorph para-laurionite.* In the literature at least 9 other references with supporting evidence for this statement have been published.

Formation of "lead"

The mechanisms proposed by Lebedev[19] and Edwards[20] could also be responsible for the formation of the lead deposit from the "oil field brine". Either directly or by exchange or adsorption processes, ^{210}Pb can be incorporated in the compound. Supporting evidence however is not available yet.

Based on lead stable isotope evidence, it appears that the brine phase plays a key role in the formation of the radioactive lead deposits. It is believed, that the lead from the brine acts as a 'carrier' for ^{210}Pb. Whether lead is actually transported with the brine or whether lead (compounds) from the brine are transported in the vapour phase, has not been confirmed yet.

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CONCLUSIONS

^{210}Pb as NORM in the gas and oil industry can have three different origins:
- supported by ^{226}Ra;
- supported by ^{222}Rn or
- unsupported.

The first two types can be easily detected in operating systems by the penetrating γ-radiation from its ancestor ^{214}Bi; the latter type cannot be detected straightforward in the field.

The only reliable method to obtain information on the presence of unsupported $^{210}Pb/^{210}Po$ in equipment, product- or waste streams in gas treating installations, is the representative sampling and subsequent analysis by well equipped, experienced radiological laboratories. In view of forthcoming (or existing) labour hygiene and environmental legislation, national authorities will require regular surveys on the radiological situation of E&P installations, on products and on waste streams. Since the European Union[22] exempt limits for $^{210}Pb/^{210}Po$ will (most likely) be in the order of 10 Bq/g, robust and verified protocols for sampling and analysis, which have been accepted by the competent authorities.

Unfortunately, no standard methods for NORM sampling in the E&P industry have been published and neither have suitable analytical procedures, for the determination of $^{210}Pb/^{210}Po$ in the matrices (various types of scale, deposits, sludges, hydrocarbon condensate, natural gas) encountered in gas and oil processing and treating, been described.

Currently, at Shell Research Amsterdam standardised sampling protocols are being investigated: standardised analytical procedures have been developed and have been discussed in our previous contribution[23].

The origin of radioactive lead compounds in equipment, products and waste streams from the gas and oil industry appears to be the brine pase, the lead from which acts as a carrier for ^{210}Pb. It is hoped to report in the near future in more detail on transport of NORM from the sub-surface to equipment and products, by-products and waste streams. When this basic knowledge has been gathered, it should be possible to invent, in a more efficient manner, means to reduce - or even prevent - the build up of NORM in the E&P industry.

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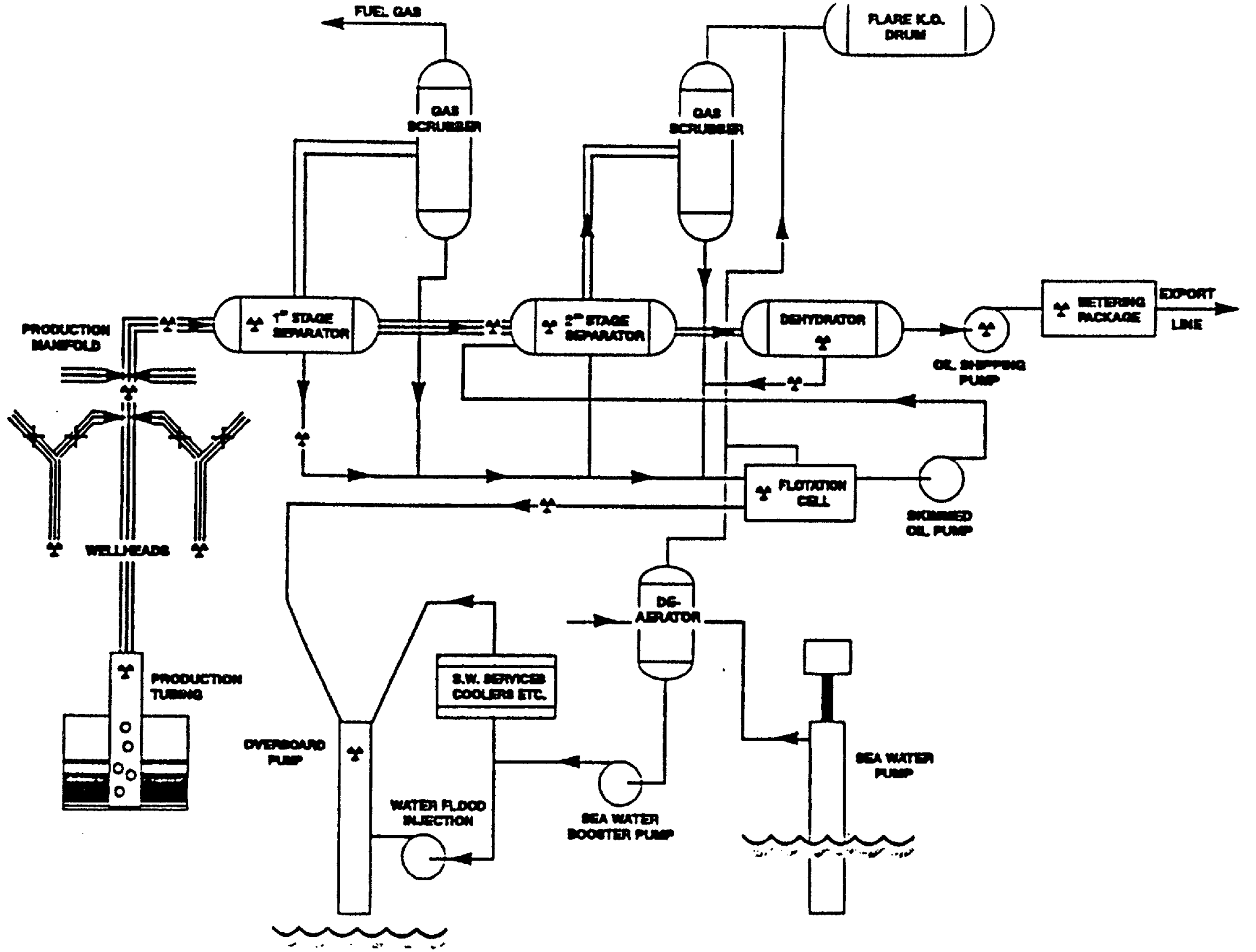

Figure 1: Simplified Off-Shore Production Train with Locations, where LSA Scale/Sludge has been found (indicated by trefoil).

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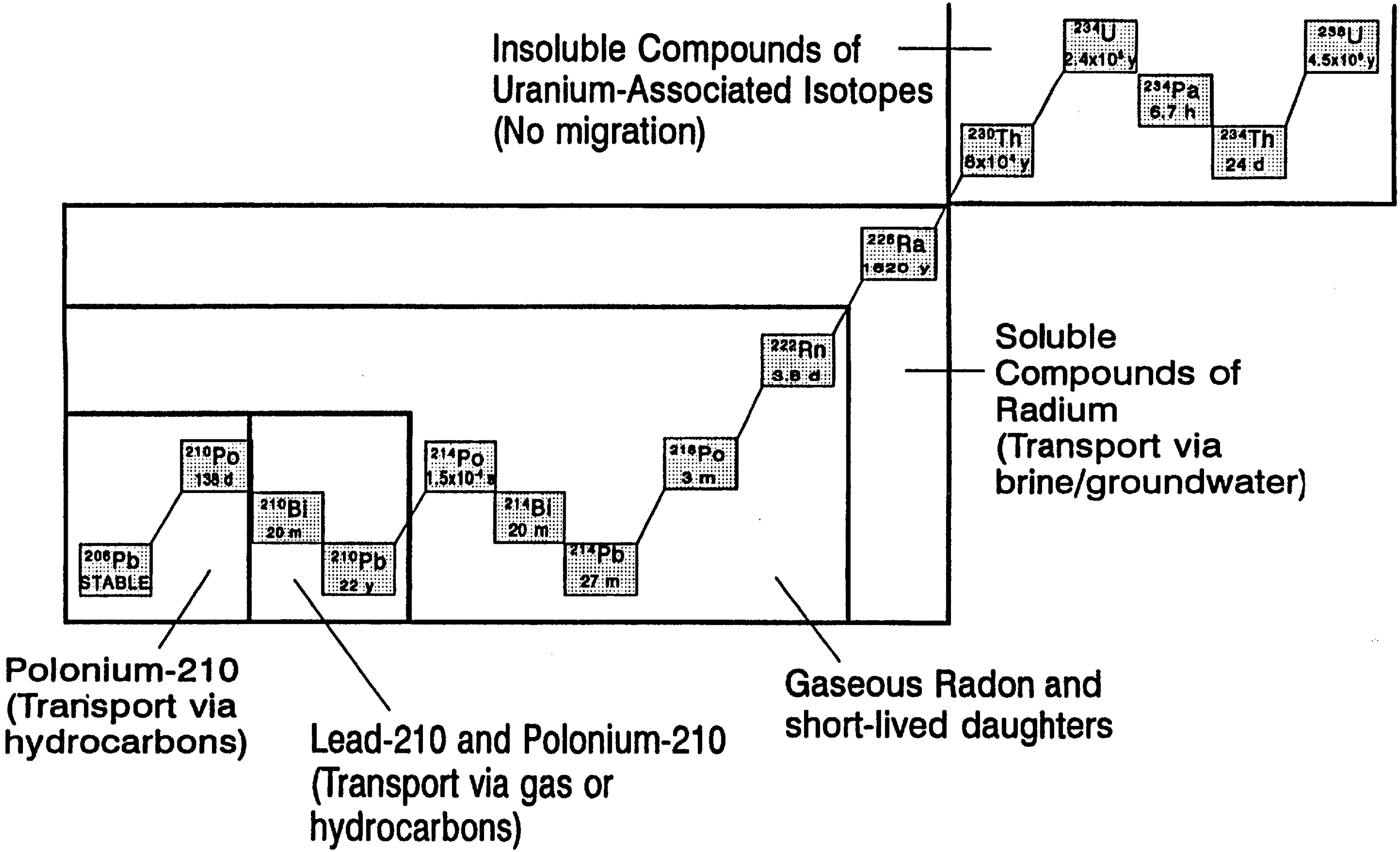

Figure 2: ^{238}U and sub-series as encounteredin E&P NORM.

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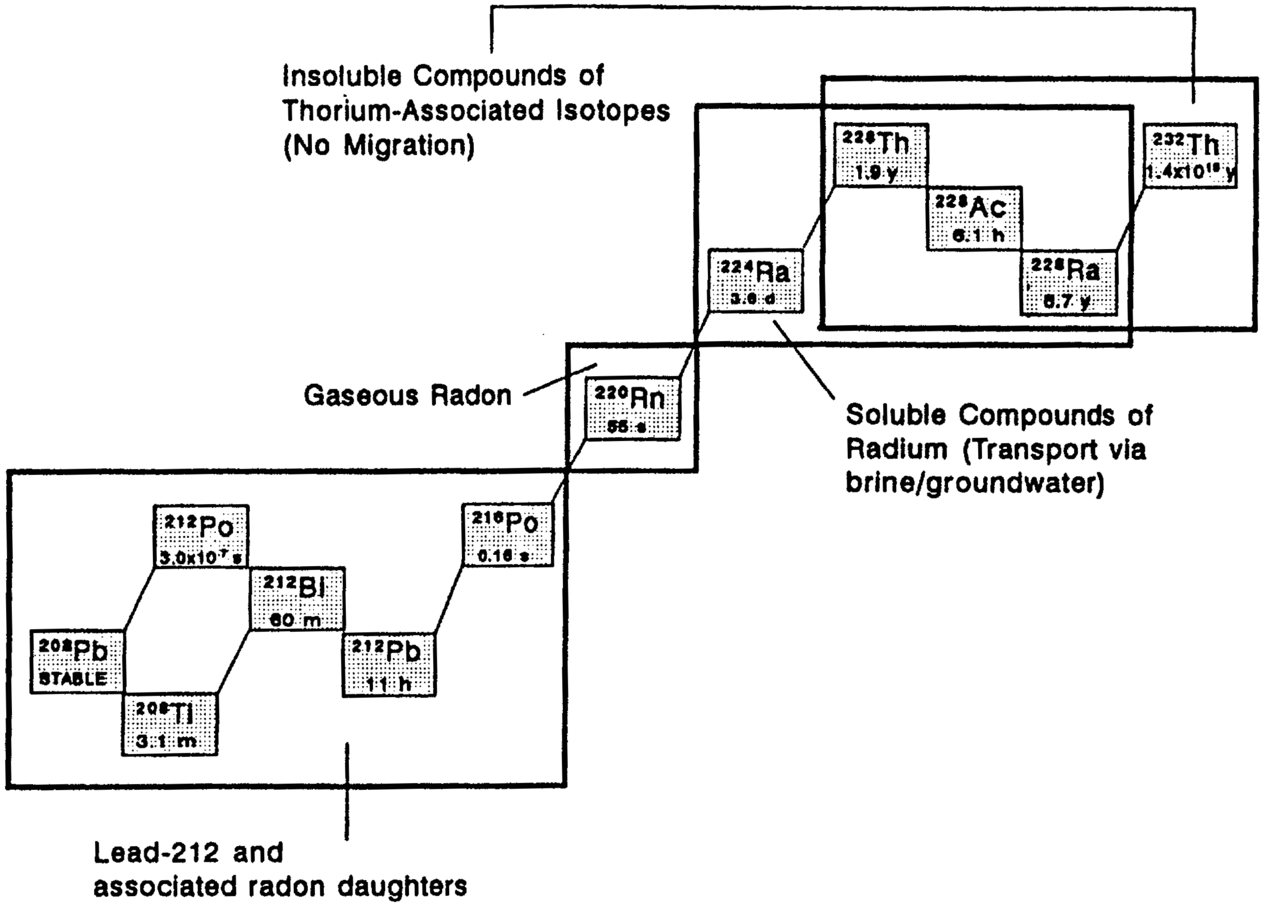

Figure 3: ^{232}Th and sub-series as encounteredIn E&P NORM.

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SESSION 2

REGULATORY ISSUES AND ACTIVITIES

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Development of a Comprehensive NORM Program

Steve Woods, Steve Abernathy, Halliburton Energy Services; Peter Johnson, CORPEX Technologies, Inc.

Abstract

Naturally occurring radioactive material (NORM) is found in some equipment and materials in the oil and gas industry. To help limit liabilities for NORM, operating companies must develop and implement a comprehensive NORM program. If a company cannot implement the required program internally, it must consider the outsourcing requirements necessary to establish a program. The five-step process (**Fig. 1, Page 2**) discussed in this paper will enable operators and service companies to

- Determine their employees current level of competence concerning NORM
- Determine what components in a NORM program are weak or lacking
- Determine which components of a NORM program will be outsourced, fully developed, or enhanced

Step 1 of this process is to secure management commitment. Management must (1) recognize the current or potential NORM liability, (2) be committed to developing a comprehensive NORM program, and (3) support the program by providing necessary resources. Once management commitment is obtained, Step 2 is to establish a NORM policy. The policy must define NORM and explain the required actions if NORM is discovered or expected.

Once a policy is established, Step 3 is to evaluate all facilities for current or potential NORM liabilities. Personnel must also be evaluated to determine their level of competence regarding NORM. Such evaluations will help the company determine the level of training that is needed or already available. During facility screenings, the company can determine the depth of the potential NORM liability and evaluate the need for other expertise.

After personnel have been evaluated and the facilities have been screened, Step 4 is to determine which activities should be kept in-house or outsourced based on capabilities, expertise, and potential liability.

Step 5, the final step, is to develop the working components of the NORM program based on the knowledge gained in Step 4. **Fig. 2, Page 3** shows the basic elements of a NORM program. In most cases, a comprehensive NORM program consists of the following items:

- Surveys—standard survey meter specifications, types of surveys, standard procedures for conducting surveys, documentation of surveys, identification and analysis of radioactive samples
- Training—awareness, surveyor, maintenance, and waste management
- Personnel monitoring (external and internal)
- Licensing—registration, general and specific
- Audit—internal and/or external
- Operating and emergency procedures
- Waste management—remediation, storage, and disposal

Introduction

Although NORM was considered a potential problem in Canada as early as 1904, it did not become a regulatory issue in the United States until 1986. That year, a highly publicized incident demonstrated that the public had been exposed to a great deal of oilfield equipment that had varying degrees of NORM contamination.[1] Since that time, several states, most notably Louisiana, Mississippi, and Texas, have established rules and regulations regarding NORM.

As a general rule, any process that extracts raw minerals and processes them to remove impurities can concentrate NORM; this concentrated or altered NORM is commonly referred to as technologically enhanced natural radioactive (TENR) material.[2]

The purpose of this paper is to provide information that will serve as a general guide to anyone who is evaluating or establishing a NORM radiation protection program.

References at the end of the paper.

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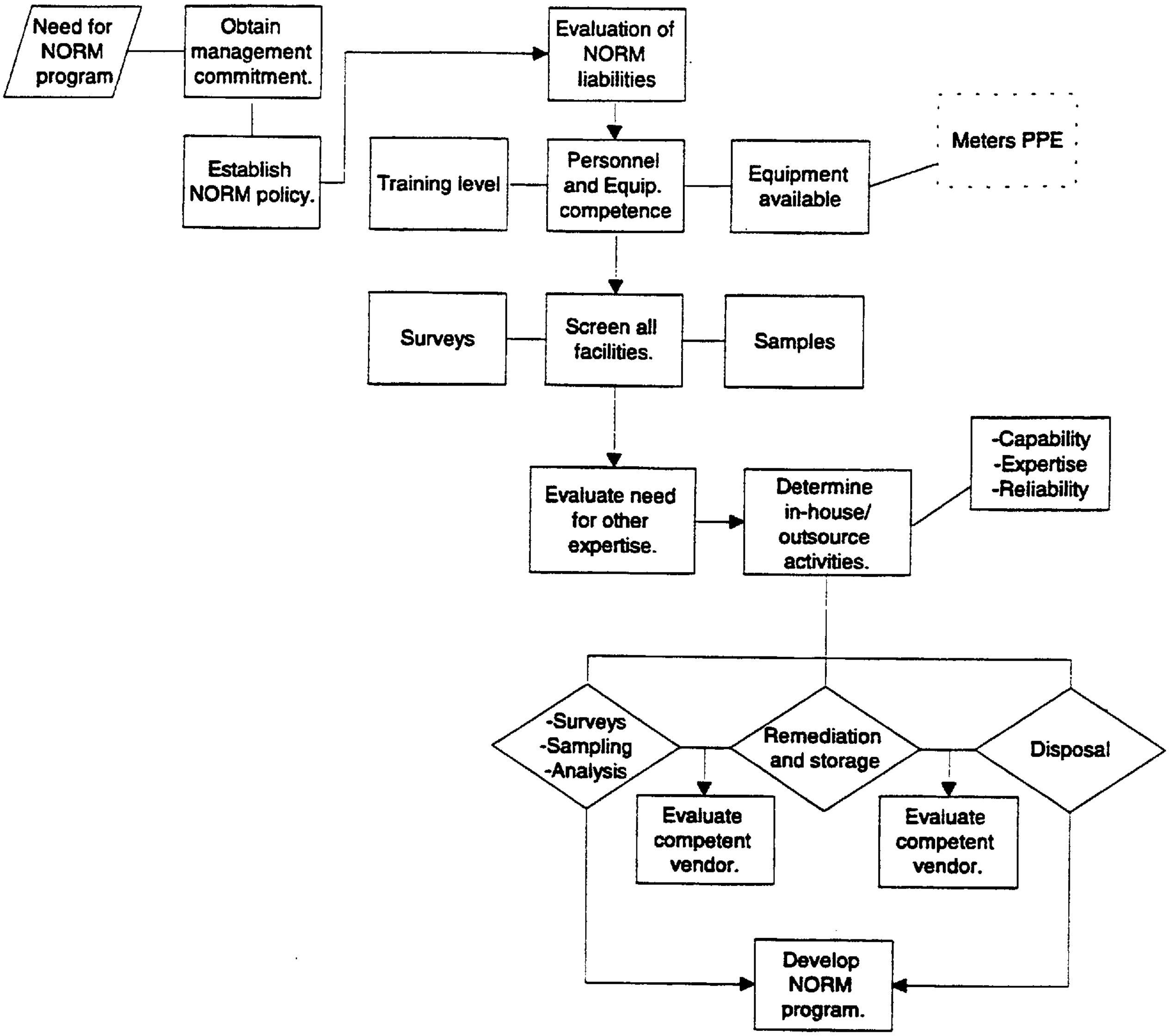

Fig. 1—NORM program evaluation.

Discussion—The Five Steps

Step 1: Obtain Management Commitment. Before management can justify expending resources, they must understand the potential for liability regarding NORM. Preliminary screening may have to be conducted to identify the liability that exists. Once management provides their commitment, a NORM policy can be established.

Step 2: Establishing a NORM Policy. A comprehensive NORM policy defines NORM and discusses where it is encountered. Such a policy would establish limits for equipment, facilities, and personnel. These limits must reflect either local regulatory requirements or a company standard that meets the minimum regulatory limit to be encountered.

A NORM policy specifies personnel protection equipment (PPE) and identifies equipment and facility protection practices. If these guidelines are already established in other company policies, they should be cross-referenced in the NORM policy. The policy should also include emergency contact information so that equipment, facility, and personnel contamination can be reported on a 24-hour basis.

Step 3: Evaluation of Facilities. The best way for a company to detect NORM is to conduct thorough equipment and facility surveys.[3] **Figs. 3 through 6, Pages 5 and 6,** provide a detailed description of the facility evaluation process, ranging from NORM detection to the logistics of interstate transportation of NORM-contaminated equipment. The survey and analysis equip-

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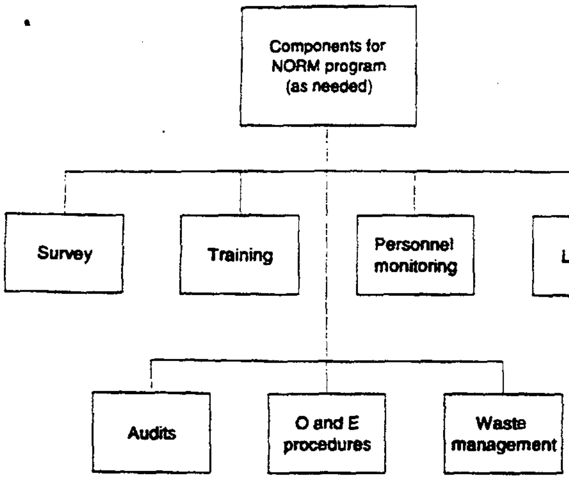

Fig. 2—Possible components of a NORM program.

ment necessary for a NORM program will vary based on the operations that are kept in-house and those that are outsourced. The personnel conducting these surveys should be adequately trained and should use compatible survey equipment to establish consistent survey results. In facilities having natural gas feedstocks, these surveys are best performed during ongoing operations. Under such circumstances, the survey equipment can be used to detect penetrating radiation found in the feedstocks but not in the residual contamination.

Screening Process. During screening, the depth of the potential NORM problem in a facility can be identified by

- gamma measurements
- alpha and beta measurements
- sample analysis

Gamma measurements. The typical survey instrument uses a sodium iodide crystal and the meter reads out in microroentgen per hour. Surveys are easier to conduct if the NaI probe is separate from the meter. This method is acceptable for checking facilities, since it indicates if there is a problem with NORM caused by most common scales.

Alpha and Beta measurements. The typical survey instrument uses a thin-window pancake probe with a meter that reads out in counts per minute (cpm). This type of instrument can also be used to check equipment and facilities. It must be used in screening if a facility has a NORM problem resulting from lead-210 and its decay products, since there would be no gamma to detect. Equipment recently removed from service or equipment that is opened for repair or cleaning can be checked at the surface to detect this type of nonpenetrating radiation. If wipes will be analyzed, a scaler or multichannel analyzer will be necessary.

Some NORM programs incorporate a detector that consists of a μR/hr and cpm dial face, a sodium iodide detector, and a pancake detector. This system allows the user to monitor alpha, beta, and gamma with one meter, eliminating the need for additional meters, calibrations, and maintenance. Air samplers and other PPE may also be required.

Sample Analysis. If elevated levels are found during screening with the meters, samples must be obtained and analyzed to determine the radionuclide and the activity. Most companies do not have the necessary equipment to analyze samples; therefore, sample analysis is usually outsourced to a qualified laboratory.

Once the presence of NORM is verified, every aspect of the business must be thoroughly evaluated to determine at what point NORM is encountered and what processes tend to concentrate it. The two primary areas to consider are employee exposure (Fig. 3) and environmental contamination (Fig. 4). Evaluators must determine if employees could ingest or inhale NORM at the areas in which NORM is found.[3] They must also determine whether the NORM is contained so that it does not escape to surrounding environments (Figs. 5 and 6).[3]

Step 4: Determine Level of Personnel Competence and Equipment Capabilities. As previously stated, personnel actively involved in the NORM program must have the proper survey equipment and be adequately trained to operate it. They must also be familiar with handling samples and should be supplied with all necessary personal protective equipment (PPE). If routine maintenance will involve NORM contact, all affected employees will require special training and equipment.

Depending on the NORM liability (or potential liability) and the company's knowledge of the NORM situation at their locations, a company may choose to outsource their NORM program until it would be more cost-effective to provide in-house training and equipment.

Step 5: Operational Requirements. Step 5 focuses on the operational requirements of a working NORM program including organization, staffing, equipment requirements, operating procedures, NORM radiation protection personnel functions, and other necessary components to a NORM radiation protection program.

Organization. If it does not already exist, a radiation safety committee should be established. Depending on the size and organization of a company, this committee should at least include a representative of senior management, an HSE representative, the personnel responsible for NORM radiation protection, and other necessary operational personnel. The primary objective of this committee is to develop and maintain an effective NORM radiation protection program.[4]

Unless an organization is unusually large, its HSE program probably lacks personnel qualified in radiation protection. If expertise does not exist, additional training may be required to qualify staff members for the regulatory requirements necessary to establish a radiation safety officer (RSO).

The RSO supervises the daily operation of the NORM program to ensure that employees, visitors, contractors, the facilities, and the public are protected from NORM above regulatory limits. Depending on the extent of the NORM pro-

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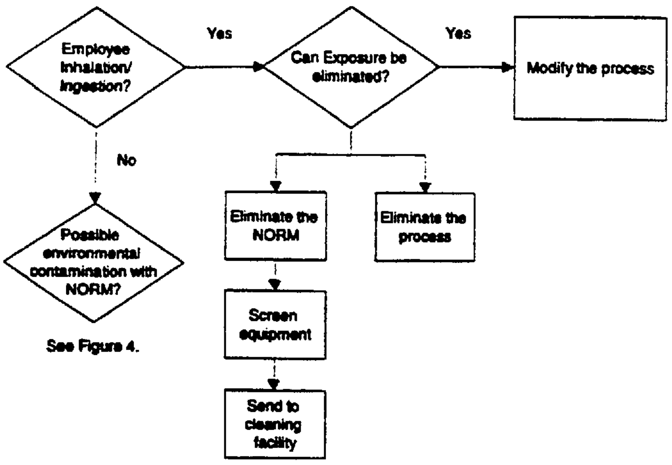

Fig. 3—Employee exposure.

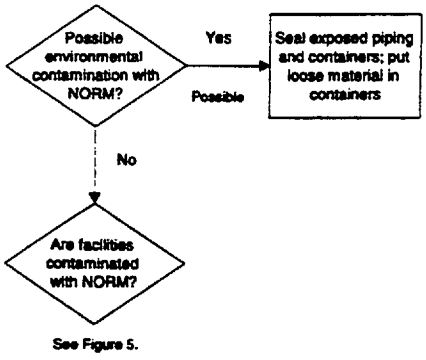

Fig. 4—Environmental contamination.

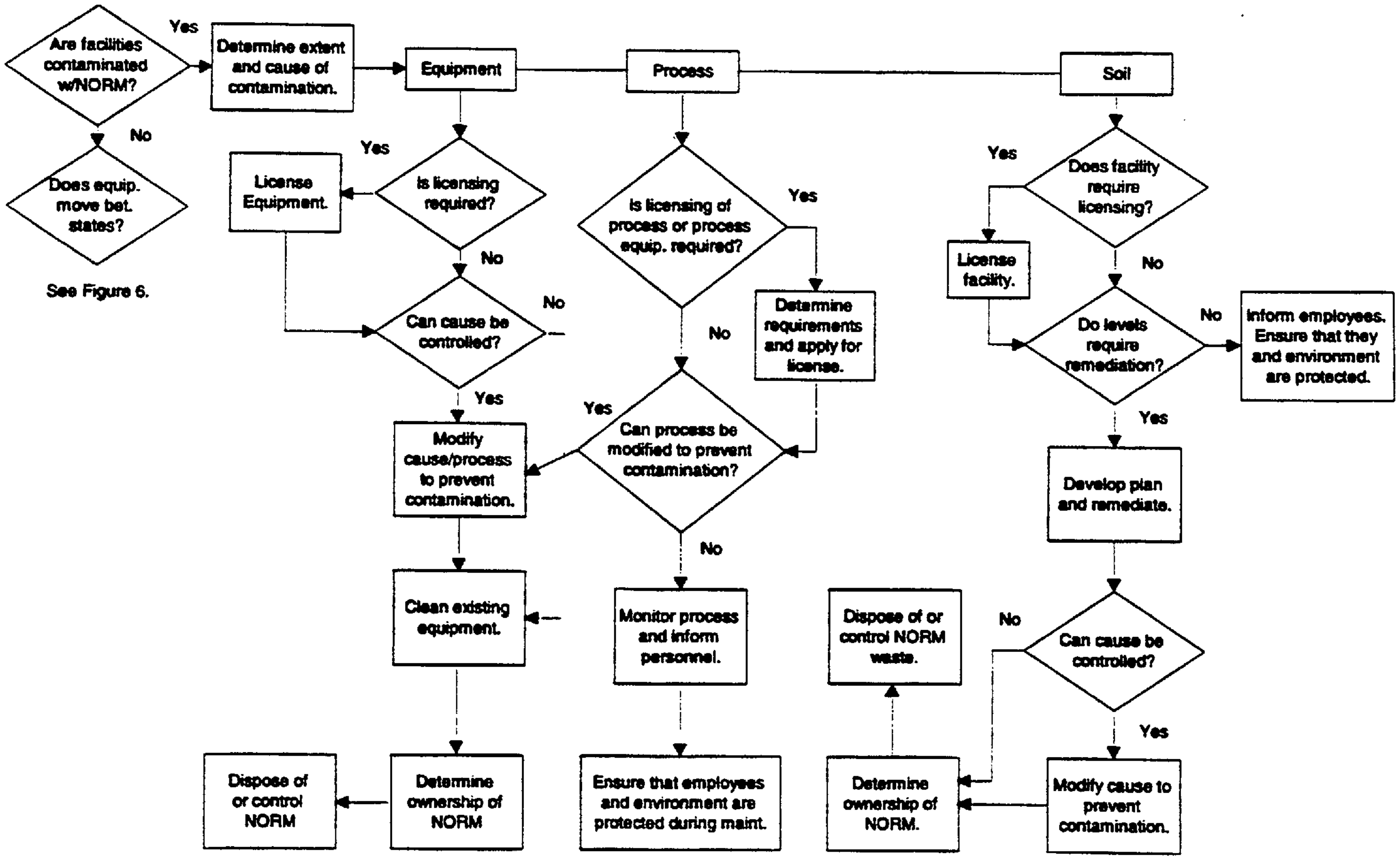

Fig. 5—Facility and equipment contamination.

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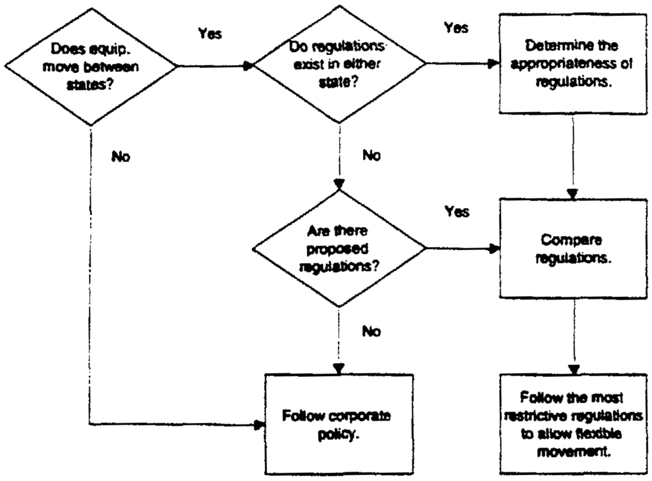

Fig. 6—Logistics of moving NORM-contaminated materials between facilities covered by different regulations.

gram, the routine responsibilities of the RSO include licensing, inventory control, NORM decontamination, radiation and contamination surveys, waste removal, storage, processing and possible disposal, equipment calibrations, personnel monitoring (external and internal), training, routine auditing and inspections as required, regulatory review, recordkeeping, and other regulatory requirements.[4]

The number of personnel required to properly administer a NORM program will vary depending on the number of facilities, the extent of NORM liabilities as established in Step 3, the complexity of operations, and the operations that were kept in-house and not outsourced.

A radiation safety manual must be developed to clarify the policies and procedures of the company's NORM program. This manual should detail management's commitment to ALARA (as low as reasonably achievable) mandates and should provide details as to who is or needs to be RACI (responsible, accountable, consulted, informed). Separate sections should provide information about training, personnel monitoring and exposure evaluation, personnel protective equipment requirements, restricted and unrestricted area operational policies, radiation survey and evaluation programs, surface contamination and evaluation programs, contamination control programs, NORM sampling programs, labeling and posting programs, inventory and control of NORM-contaminated equipment, the service and maintenance of NORM-contaminated equipment, NORM-generated waste management programs, NORM packaging and transportation programs, NORM records management programs, and NORM incident and emergency response procedures.

Standard operating procedures (SOPs) for all operations must also be written. These detailed SOPs should include decontamination of equipment and facilities, decontamination of land, encapsulation, processing, storage, and disposal information.

Functions. Among other minor responsibilities, the functions of the NORM RSO include licensing, training, remediation and decontamination review, personnel monitoring, bioassay, surveys, sampling, inventory control, disposal, meter calibrations audits, and emergency response.

Licensing may include general and possibly specific licenses depending on the state and the degree to which the NORM program will be established. Licensure will require some type of regulatory approval, and all the requirements are usually established in some type of regulatory guide.

The NORM RSO should either conduct training programs or coordinate the training for maintenance personnel and others on an as-needed basis. Additionally, the RSO should establish and monitor some type of NORM awareness program for all employees. With the possible exception of awareness programs, most NORM training programs will require regulatory approval. Companies should be cautious about providing in-house training on radiation protection for workers when no regulatory requirements are set. Such a situation could result in legal action if key components of the training program are found to be subsequently left out of the training.

Personnel monitoring is required for persons who could potentially receive over 10% of the permissible limit for external radiation.[5] This requirement can be met with the use of thermoluminescent dosimeters (TLDs), which are usually exchanged with a regulatory-approved vendor on a quarterly basis. Depending on the regulatory requirements and the type of work being conducted, bioassay may be required of some workers. External and internal personnel monitoring requires a great deal of paperwork. In 1993, a major regulatory change required licensees to sum the "total effective dose equivalent" of external and internal doses.

Routine facility, site, and equipment surveys must be conducted, documented and maintained. Contaminated equipment that is kept in service must be inventoried and tracked so that it can be decontaminated before servicing. If decontamination is not practical, service personnel should be notified of the contamination so that they can take the proper precautions.

The survey frequency will be dictated by regulatory requirements or company policy. While workers could be trained to conduct some routine surveys, the NORM RSO should conduct routine surveys and special surveys, such as air sampling and final-release surveys. Additionally, the RSO should collect and analyze environmental samples to establish an ongoing database of sampling data. This database will help establish baselines on new facilities and clearance for old facilities.

The RSO ensures and verifies that all survey meters, air samplers, and other equipment are calibrated as required by regulation. The RSO also coordinates waste disposal and emergency response. These issues, however, are beyond the scope of this presentation.

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Conclusion

All major components of an organization will have a role in developing and implementing a comprehensive NORM program. Therefore, a NORM task force should be comprised of not only health and safety representatives but also representatives from management, research and engineering, and operations. Each different group brings different skills, process knowledge, and expertise that are essential to providing a safe, efficient NORM program. Such a program should incorporate all the main ideas discussed in this paper. When properly implemented among all parts of an organization, a NORM program provides the stability and means for accurate, reproducible data, worker and facility protection, and environmental protection.

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Transportation Regulations for LSA NORM

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and
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Research and Special Programs Administration
U.S. Department of Transportation
Washington, DC

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When is Material in Transport Regulated as Hazmat?

- Does the material meet the definition of a hazardous material in the regulations?
- Is the movement within the definition of transportation?
- Does the activity involve **commerce**?

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Present Definition of Radioactive Material for Transport Regulations

Domestic

- DOT

International

- IAEA, IMO, ICAO,

0.002 uCi/g, 2 nCi/g, 2,000 pCi/g
(70 Bq/g, 70 kBq/kg)

Same value for each radionuclide, or for mixtures of radionuclides.

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Definition will be Replaced by Exemptions in 1996 IAEA Regulations

Transportation will use same standard used for other practices (S.S. No. 115-I).

Exemption Values for every radionuclide

- activity per gram of material; OR
- total activity in package/shipment.

Examples of exempt quantities

Th-230	1 Bq/g and 1 x 10^4 Bq	Ac-227	0.1 Bq/g and 1 x 10^2 Bq
Ra-226	10 Bq/g and 1 x 10^4 Bq	I-131	100 Bq/g and 1 x 10^6 Bq
Co-60	10 Bq/g and 1 x 10^5 Bq	H-3	1 x 10^6 Bq/g and 1 x 10^9 Bq

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Some Actions Involving NORM Probably will be Exempted in 1996 IAEA Regulations

Draft statement for exempted materials:

> "Natural material and ores which contain naturally occurring radionuclides, in unmodified or decreased concentrations and which are not intended to be processed to use these radionuclides."

Nuclear fuel cycle practices will not be exempted.

National authorities will regulate practices and materials, as appropriate.

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DOT Rules Prior to HM-169A (9/28/95)

LSA materials include:

- o materials containing dispersed activity.
- o non-radioactive objects with radioactivity on surfaces.

Packages containing less than A_2 quantities transported in:

- o DOT Spec. 7A Type A (non-exclusive use).
- o strong tight packages (exclusive use).
    - materials with low specific activity.
    - objects with surface contamination.
- o lower level, bulk closed vehicles or tanks (exclusive use).

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New DOT Rules Impacts on NORM

Permitted November 1, 1995 -- Required April 1, 1996

Domestic rules consistent with international rules (IAEA, IMO, and ICAO).

New classification and packaging for low-level materials (some A_2 values changed (radium increased)).

Use of international radiological units.

Radiation protection must be considered.

Many requirements are unchanged.

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New HM-169A Rules for LSA

LSA-I, LSA-II, and LSA-III for materials with radioactivity throughout.

SCO-I and SCO-II -- radioactivity on outer or inner surfaces of non-radioactive objects.

LSA or SCO unpackaged cause less than 1 R/h @ 3 m.

Packaging as before -- Type A, strong tight or bulk; OR Industrial packages (IP-1, IP-2, or IP-3).

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LSA-I

Lowest level material with activity throughout.

Materials containing radionuclides with unlimited A_2 values.

Uranium and thorium ores and concentrates.

Soil, rubble, debris, and tailings with radionuclide concentrations less than $10^{-6}\,A_2/g$.

Transport: bulk or strong tight packages (exclusive use), or IP-1 (exclusive use or non-exclusive use).

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LSA-II

Tritiated water with concentration up to 0.8 TBq/l (20 Ci/l)

Materials for which the radioactivity is uniformly distributed and with specific activity limited to:

- 10^{-4} A_2/g for solids and gases
- 10^{-5} A_2/g for liquids

Transport: strong tight packages (exclusive use), DOT Spec. 7A Type A (non-exclusive use), for solids IP-2 (exclusive use or non-exclusive use), or for liquids IP-2 (exclusive use) or IP-3 (non-exclusive use).

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LSA-III

Solid, non-leachable materials with average specific activity less than 2×10^{-3} A_2/g.

Transport: DOT Spec. 7A Type A or IP-3 (non-exclusive use), or strong tight or IP-2 (exclusive use).

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SCO-I

Accessible surface limits:

- o Fixed - 0.04 MBq/cm^2 (1 uCi/cm^2) beta-gamma or 0.004 MBq/cm^2 (0.1 uCi/cm^2) alpha.
- o Non-fixed - 4 Bq/cm^2 (0.1 nCi/cm^2) beta-gamma or 0.4 Bq/cm^2 (10 pCi/cm^2) alpha.

Inaccessible surface limits:

- o Fixed plus non-fixed - 0.04 MBq/cm^2 (1 uCi/cm^2) beta-gamma or 0.004 MBq/cm^2 (0.1 uCi/cm^2) alpha.

Transport: bulk or strong tight packages (exclusive use), or IP-1 (exclusive use or non-exclusive use)

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SCO-II

Accessible surface limits:

- Fixed - 0.74 MBq/cm^2 (20 uCi/cm^2) beta-gamma or 0.074 MBq/cm^2 (2 uCi/cm^2) alpha.
- Non-fixed - 400 Bq/cm^2 (10 nCi/cm^2) beta-gamma and 40 Bq/cm^2 (1.0 nCi/cm^2) alpha.

Inaccessible surface limits:

- Fixed plus non-fixed - 0.74 MBq/cm^2 (20 uCi/cm^2) beta-gamma or 0.074 MBq/cm^2 (2 uCi/cm^2) alpha.

Transport: strong tight package or IP-2 (exclusive use), or DOT Spec. 7A Type A or IP-3 (non-exclusive use).

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Bulk Transport by Vessel

Title 46 CFR Part 148 (Coast Guard regulations)

- o old LSA rules - limit on Transport Group I nuclides
- o shipping documents, no marking or labeling, clean after use.

IMO Solid Bulk Cargo Supplement, Appendix B

- \- LSA-I and SCO-I only

IMDG requirements applicable such as documentation, cleanliness, stowage, etc.

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SESSION 3

NORM MANAGEMENT AND DISPOSAL

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Effective Removal of NORM Scale in the Rycroft Field

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Abstract

A recent field case history is presented that demonstrates how solvent was used to effectively remove $BaSO_4$ scale that was contaminated with naturally occurring radioactive material (NORM). A compositional water analysis was used to pinpoint the source of the scale and deposition tendencies. Field laboratory data were used to specify the treating schedule, including volumes and contact time. The treated well was an injector for a waterflood project. Injection rate and wellhead pressure profiles from January 1994 to June 1995 demonstrate the removal of scale as a result of the solvent operation. Pre- and post-treatment gamma ray spectroscopy logging data document the effectiveness of scale removal. As a result of this research, operators can now mitigate NORM problems and in favorable circumstances, eliminate the need for costly NORM disposal.

Introduction

Scale is a solid mineral deposit usually formed from produced salt water.[1] Because water constantly dissolves and deposits solids, scale is an endless problem in the petroleum industry. Scale occurs in primary production wells, secondary wells, injection wells, disposal wells, and pipelines that connect wells to tank batteries. Wherever water production occurs, a potential for scale formation exists.

Scale can be caused by any one or a combination of several factors, including pressure changes, temperature changes, impurities, additives, variation of flow rates, changes in pH, fluid expansion, gas evaporation, and mixing of incompatible waters. The mixing of incompatible waters causes the minerals in solution to form an insoluble precipitate, which then deposits in the wellbore or the well pump. Scale can develop almost immediately, or it can build up over several months before becoming noticeable. For example, calcium carbonate develops quickly but is relatively easy to treat. In contrast, $BaSO_4$ is typically slower to form, but it is more difficult to treat.

The effects these scales have on a well depends largely on their location and the amount of scale deposited in the system. Scales can restrict and completely choke production in the tubing, in the flowlines, at the surface, or in the perforations. Scales can also deposit in fractures and formations that are distant from the wellbore.

The deposition of inorganic scale in producing wells is an expensive problem in the oil industry. Stuck downhole pumps, plugged perforations and tubing strings, choked flowlines, frozen valves, equipment damage, and downtime during maintenance all contribute to economic loss. Scale restricts production and causes inefficiency and failure of production equipment. As fields mature and require waterflood operations, the scale problems have an increased effect on well profitability. Because radioactive materials are often incorporated into scale as it forms, scale disposal usually requires special procedures and can be costly to accomplish.

Barium Sulfate

Barium sulfate ($BaSO_4$) is highly insoluble (2 mg/L in water), and usually cannot be economically dissolved by a chemical agent. In most cases, the only way to remove precipitated $BaSO_4$ is by mechanical scraping or reaming, which is troublesome and costly.

Factors for $BaSO_4$ precipitation include lower temperatures, dilution of brine content, dilution of carbonate content, and mixing of incompatible waters. The commingling of producing zones is the leading cause of $BaSO_4$ scale problems in the oil field. Because $BaSO_4$ is more soluble at higher temperatures and pressures, it is routinely encountered in waters from deeper and hotter oil wells. Water produced from deep, hot wells also tends to have elevated brine and carbonate content, both of which increase the solubility of the $BaSO_4$. As deep well fluids are produced, the subsequent drop in temperature and pressure results in the precipitation of $BaSO_4$. Produced brine fluids are

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typically reinjected as a means of disposal. Often, the brines are mixed with waters from other zones. If this water is fresh, the reduced salinity of the mixed water reduces $BaSO_4$ solubility, and scale forms.

$BaSO_4$ and strontium sulfate are often deposited together because barium and strontium have similar chemical properties. Iron is another common coprecipitate. Because of these contaminants, $BaSO_4$ scale deposits occur in a variety of colors and shapes.

NORM in Scale

Sources of NORM. NORM is common in everyday life; it is in the ground, the air, and in the body. The average person is exposed to about 100 to 300 millirems of radiation per year; half of this radiation is from natural sources.

All natural elements heavier than bismuth (^{209}Bi) are unstable. Radioactive isotopes can be grouped into a sequence of decays, so that members in each such chain constitute a radioactive family or series. The natural radioactive substances found in earth formations include three families:

- uranium
- thorium
- actinium

Uranium (^{238}U) is the parent of the uranium series. After 14 transformations, uranium reaches a stable lead isotope (^{206}Pb). This series, which includes radium (^{226}Ra) and its daughter products, is of the most concern to the petroleum industry.

Thorium (^{232}Th) is the parent of the thorium series with ^{208}Pb as its stable end-product. Its daughters include ^{228}Ra, which is of lesser concern in oil and gas operations.

The actinium series is headed by ^{235}U, but its members are not found in amounts of concern in petroleum activities. The only other naturally radioactive element is potassium (^{40}K).

Those working in certain oil and gas operations need to keep in mind that the isotope ^{226}Ra is the radioactive contaminant that occurs in some scales (usually barite). It has a half-life of 1,620 years and obviously will not decay perceptibly in the timeframe of typical oilfield operations. It decays to the noble gas radon (^{222}Ra), which has a half-life of about 92 hours. Gaseous radioactive radon can be hazardous in some circumstances, but it is trapped in the crystal lattice in scales such as barite. Its daughters, ^{214}Bi and ^{214}Pb, give rise to practically all the gamma radiation from NORM-contaminated scale.[2]

Regulation of NORM. Radioactive materials are categorized by the amount of radiation they are likely to produce. NORM scale is categorized as a potential hazard.

In the oil industry, NORM occurs in the scale that clogs pipes and equipment and in the sludge from the bottom of oil storage tanks. Although health risks from the low levels of radiation in NORM are thought to be minimal, disposal of NORM wastes can create greater hazards. For instance, the radioactivity from oilfield scale is usually very low from pipe to pipe, but the total radiation level increases when all the pipe scale at one site is gathered in one place.

Since the introduction of regulations concerning NORMs, disposal of oilfield scale, particularly $BaSO_4$, has become increasingly troublesome and expensive.

As of July 1994, the only site available for NORM waste disposal in the United States was in Utah at a cost of $300 to $500 per drum. The Environmental Protection Agency (EPA) has allowed some operators to pump NORM materials underground in suitable hazardous waste disposal wells.

NORM scale is regulated by individual states under Subtitle D of the Resource Conservation and Recovery Act (RCRA) as a solid waste under the drilling fluids exclusion. Texas and Louisiana implemented their own regulations. In Louisiana, equipment and piping can be used without restriction if the maximum radiation exposure level does not exceed 25 microrems/hour, according to *Implementation Manual for Management of NORM in Louisiana*. The maximum contact reading for Texas is 50 microrems/hour, according to *Texas Regulations for Control of Radiation, Part 46*. Several other states follow the Texas regulation. Most oil- and gas-producing nations have established NORM contamination standards and procedures since the material was recognized as a problem in the North Sea in 1981.[3]

Well and Completion Data

The well treated in this study was completed in October 1984. The elevation used as a reference point was the kelly bushing (KB) at 642.90 m. The well had a total depth of 1445.0 m with a plugged-back total depth of 1429.0 m. A 219-mm, 35.7-kg/m, J-55 surface casing was landed at 214 m. The production casing, 140-mm, 20.8-kg/m, K-55, was landed at 1441.0 m and cemented. The perforated interval was 1369.0 to 1372.0 m. This zone was perforated on October 11, 1984 with a 102-mm casing gun. The perforated interval contained 13 shots per meter. The well was converted to an injector on November 12, 1985. Tubing used in the well consisted of 73-mm, 9.67-kg/m, J-55, EUE, TK-99 internal coating. Setting depth of the total string was 1366.45 m.

A gelled acid wash and squeeze with 1.4 m^3 of 15% HCl and 4 m^3 of gelled 28% HCl was performed in October 1984. A nitrogen squeeze was performed at 500 to 900 scf/min at 23 MPa on December 21, 1985. Five solvent treatments were performed on the well between May 27, 1988 and June 16, 1992. An acid wash and squeeze were performed on July 26, 1993. A static bottomhole pressure of 10 985 kPa and a static bottomhole temperature of 53°C were measured on November 8, 1985. The estimated relative density of the water was 1.019 and the estimated relative density of the gas was 0.660.

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Table 1—Analysis of Produced Water[a]

Specific Gravity	1.025
pH	7.42
Resistivity	0.20

Ion	Concentration mg/L
Carbonate (CO_3)	0
Bicarbonates (HCO_3)	740
Chlorides (Cl)	21 200
Sulfate (SO_4)	12 020
Strontium (Sr)	54
Barium (Ba)	1
Calcium (Ca)	1260
Magnesium (Mg)	224
Sodium (Na)[b]	13 400
Iron (Fe)	1
Total Dissolved Solids (TDS)	39 100

[a] Sample analyzed according to API RP for analysis of Oilfield Waters, July 1981.

[b] Determined by ionic balance. Resistivity has units of ohm/m^2/m

Table 2—Analysis of Source Water[a]

Specific Gravity	1.025
pH	7.81
Resistivity	0.30

Ion	Concentration mg/L
Carbonate (CO_3)	0
Bicarbonates (HCO_3)	453
Chlorides (Cl)	14 700
Sulfate (SO_4)	1
Strontium (Sr)	50
Barium (Ba)	119
Calcium (Ca)	311
Magnesium (Mg)	117
Sodium (Na)[b]	8790
Iron (Fe)	1
Total Dissolved Solids (TDS)	24 600

[a] Sample analyzed according to API RP for analysis of Oilfield Waters, July 1981.

[b] Determined by ionic balance. Resistivity has units of ohm/m^2/m

Water Analysis and Scaling Tendencies

Scale formation was thought to be the cause for decline of injection rate in the well. The assumption was made that the mixing of incompatible waters was the reason for scale formation. The produced water and source water were analyzed, and the scaling tendencies of the individual waters and both waters mixed in various ratios were calculated over a range of applicable temperatures.

Water Analysis. Tables 1 and 2 show complete analyses of the produced water and the source water. The produced water was high in sulfate while the source water was high in barium. These results suggest that $BaSO_4$ scale could form if the two waters were mixed.

Scaling Tendencies. Scaling tendencies for both the produced water and the source water were calculated with a scale measurement computer program (Program 1). This scale program calculated the tendency of the water to form calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), $BaSO_4$, and strontium sulfate ($SrSO_4$) scales at 24°, 38°, 52°, and 66°C. Results are shown in **Tables 3 and 4, Page 4.**

The program indicated that the produced water had a strong tendency to form $CaCO_3$ scale at 24° to 66°C, a slight tendency to form $BaSO_4$ scale at 24° to 52°C, and a slight tendency to form $SrSO_4$ scale at 38° to 66°C.

The source water showed a moderate tendency to form $CaCO_3$ scale at 24° to 66°C and a slight tendency to form $BaSO_4$ scale at 24° to 52°C.

Another scale measurement program (Program 2) was used to calculate the scaling tendency of two waters mixed together at various ratios at a single temperature. $CaCO_3$, $CaSO_4$, $BaSO_4$, and $SrSO_4$ tendencies were calculated at 24°C. Program 2 was run at 24° and 53°C. Various ratios of the produced water and source water at 24°C showed a moderate to strong tendency to form calcium carbonate scale and slight to strong tendency to form $BaSO_4$ scale. Identical results were produced when Program 2 was run at 53°C. Results are displayed in **Tables 5 and 6, Page 5.** Whenever the produced water and the source water were mixed together, $CaCO_3$ or $BaSO_4$ scale was more likely to form.

Compositional and Analytical Tests of Scale

As stated previously, the injection rate had slowly declined in the water injection well. This decline was most likely the result of scale buildup caused by the mixing of incompatible waters. Before an effective scale removal procedure could be implemented, more information about the scale was required.

Compositional Analysis. After a scale sample was obtained from the well, X-ray diffraction (XRD) techniques were used for mineral identification. The analysis indicated that $BaSO_4$ was the only crystalline mineral present.

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Table 3— Scaling Tendency in Produced Water (Program 1)

Type of Scale	Scaling Tendency	Scale lb/Mbbl
24°C		
Calcium Sulfate	None	0
Calcium Carbonate	Strong	295
Barium Sulfate	Slight	1
Strontium Sulfate	None	0
38°C		
Calcium Sulfate	None	0
Calcium Carbonate	Strong	152
Barium Sulfate	Slight	1
Strontium Sulfate	Slight	2
52°C		
Calcium Sulfate	None	0
Calcium Carbonate	Strong	391
Barium Sulfate	Slight	1
Strontium Sulfate	Slight	5
66°C		
Calcium Sulfate	None	0
Calcium Carbonate	Strong	413
Barium Sulfate	None	0
Strontium Sulfate	Slight	8

Table 4—Scaling Tendency in Source Water (Program 1)

Type of Scale	Scaling Tendency	Scale lb/Mbbl
24°C		
Calcium Sulfate	None	0
Calcium Carbonate	Moderate	103
Barium Sulfate	Slight	1
Strontium Sulfate	None	0
38°C		
Calcium Sulfate	None	0
Calcium Carbonate	Moderate	152
Barium Sulfate	Slight	1
Strontium Sulfate	None	0
52°C		
Calcium Sulfate	None	0
Calcium Carbonate	Moderate	182
Barium Sulfate	Slight	1
Strontium Sulfate	None	0
66°C		
Calcium Sulfate	None	0
Calcium Carbonate	Moderate	218
Barium Sulfate	None	0
Strontium Sulfate	None	0

Next, a scanning electron microscope (SEM) with an X-ray energy spectrometer (XES) was used to determine the elemental composition of the sample. Barium (Ba) was the predominant element with lesser amounts of sulfur (S). Trace quantities of iron (Fe), calcium (Ca), strontium (Sr), and aluminum (Al) were also detected. Results are displayed in **Figure 1**.

Scale Solubility. For gravimetric solubility tests, 0.7g of the scale was combined with 100 mL of a specific fluid system. The samples were then placed in a constant-temperature water bath at 60°C for 60 hours. The samples were removed from the bath at the end of the test period and the remaining scales were dried in a vacuum oven and weighed. The percentages of solubility are listed in **Table 7**. Maximum solubility of the scale was obtained with a fluid system consisting of 30% water and 70% $BaSO_4$ scale solvent. As predicted, the scale showed no solubility in 15% HCl and 12% HCl-3% HF.

Treatment and Verification History

Summary of Treatment Decisions. $BaSO_4$ scaling had consistently decreased injectivity and increased costs to support the waterflood. Difficulty in maintaining injection had resulted in increased gas/oil ratios, which jeopardized the pool's operation. The injection well had received a total of eight treatments in the last 10 years. Conventional mechanical removal of the $BaSO_4$ scale would result in radioactive material being circulated back to the surface. Pretreatment gamma ray spectroscopy logging determined the location and amount of $BaSO_4$ scale. Pretreatment laboratory testing determined the concentration and contact time required for the $BaSO_4$ scale solvent treatment. The injection rate before the treatment was less than12 m^3/day at 16,050 kPa wellhead pressure.

Pre- and Post-Treatment Gamma Ray Spectroscopy Measurements. Pre- and post-treatment measurements were performed with a wireline gamma ray spectroscopy instrument to verify the scale treatment results. The gamma ray analysis log **(Figure 2, Page 6)** shows a track of gamma ray data on either side of the depth track. The track on the left side of the figure shows an openhole gamma ray log obtained before the well was cased. This data was corrected to cased-hole conditions and used to subtract the natural background from the gamma ray signal caused by the scale in this well. Note that the perforated interval at 1369 to 1372 m is immediately below an organic-rich shale, where the relatively high gamma ray signal is the result of uranium. This uranium was discovered during earlier gamma ray spectroscopy measurements in this field.

A bridge plug was set at 1364 m. After the treatment, the bridge plug was removed and the well was cleaned up. A post-treatment gamma ray spectroscopy log was then run. The right side of the gamma ray track in Figure 2 shows the NORM gamma ray signals before and after the well was treated.

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Table 5—Scaling Tendency at 24°C (Program 2)

Water Ratios Prod/Source	Calcium Carbonate		Calcium Sulfate		Barium Sulfate		Strontium Sulfate	
	Tendency	Scale[a]	Tendency	Scale[a]	Tendency	Scale[a]	Tendency	Scale[a]
100:0	Strong	295	None	0	Slight	1	None	0
90:10	Strong	279	None	0	Moderate	7	None	0
80:20	Strong	262	None	0	Strong	14	None	0
70:30	Moderate	245	None	0	Strong	21	None	0
60:40	Moderate	227	None	0	Strong	28	None	0
50:50	Moderate	212	None	0	Strong	35	None	0
40:60	Moderate	195	None	0	Strong	42	None	0
30:70	Moderate	176	None	0	Strong	50	None	0
20:80	Moderate	156	None	0	Strong	57	None	0
10:90	Moderate	132	None	0	Strong	63	None	0
0:100	Moderate	103	None	0	Slight	1	None	0

[a] in units of lb/Mbbl.

Table 6—Scaling Tendency at 53°C (Program 2)

Water Ratios Prod/Source	Calcium Carbonate		Calcium Sulfate		Barium Sulfate		Strontium Sulfate	
	Tendency	Scale[a]	Tendency	Scale[a]	Tendency	Scale[a]	Tendency	Scale[a]
100:0	Strong	395	None	0	Slight	1	Slight	5
90:10	Strong	378	None	0	Moderate	7	Slight	3
80:20	Strong	361	None	0	Strong	14	None	0
70:30	Strong	344	None	0	Strong	21	None	0
60:40	Strong	326	None	0	Strong	28	None	0
50:50	Strong	308	None	0	Strong	35	None	0
40:60	Strong	289	None	0	Strong	42	None	0
30:70	Strong	270	None	0	Strong	49	None	0
20:80	Moderate	248	None	0	Strong	56	None	0
10:90	Moderate	221	None	0	Strong	63	None	0
0:100	Moderate	187	None	0	Slight	1	None	0

[a] in units of lb/Mbbl.

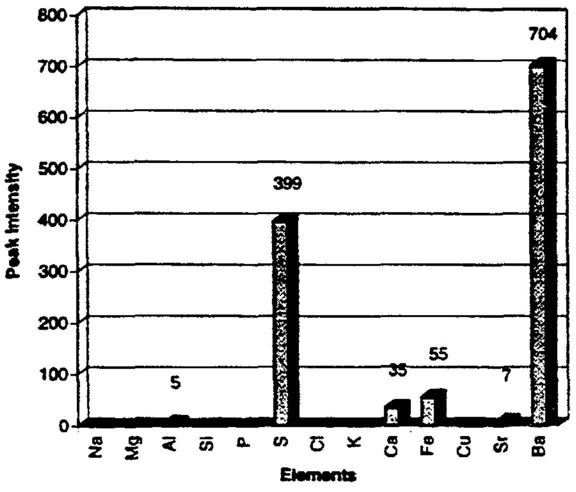

Fig. 1—Elemental analysis from X-ray energy spectrometer (XES).

Table 7—Barium Sulfate Scale Solubility Tests (60°C for 60 Hours)

Fluid System	% Solubility
50% H_2O/50% $BaSO_4$ Scale Solvent	75
40% H_2O/60% $BaSO_4$ Scale Solvent	86
30% H_2O/70% $BaSO_4$ Scale Solvent	99
100% $BaSO_4$ Scale Solvent	95
15% HCl	0
12% HCl–3% HF	0

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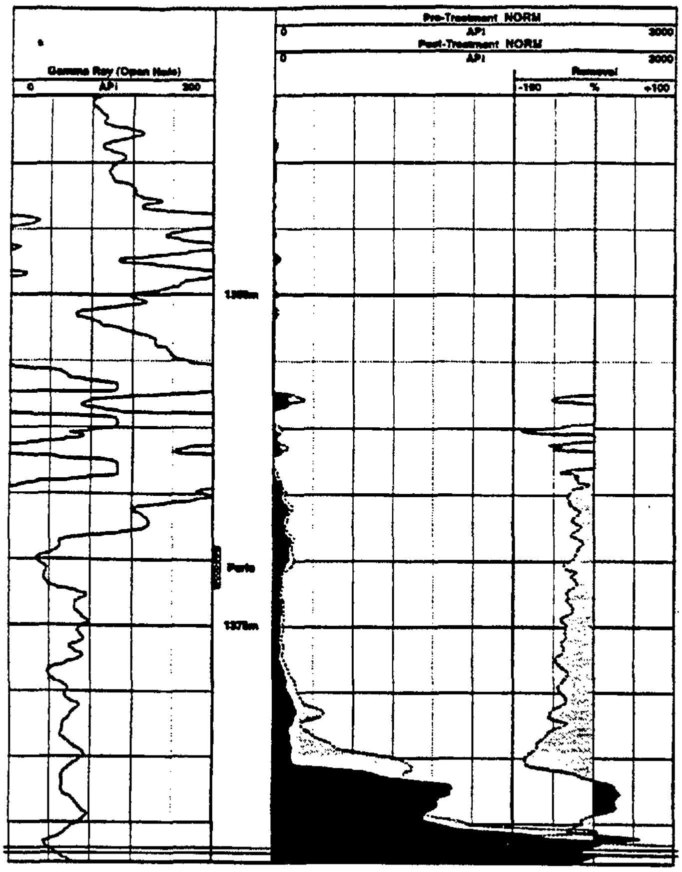

Fig. 2—Gamma ray analysis log.

The gray NORM curve is the result of the scale present before treatment. The black NORM curve represents the scale remaining after treatment. The gray shading shows the relative amount of scale removed within the depth-of-investigation of this gamma ray survey technique (0.2 to 0.3 m beyond the wellbore). The dashed curve on the right side of this track shows the relative amount of scale removed or redistributed. The gray shading indicates that 20 to 50% of the scale was removed in the interval from 1357 to 1383 m surrounding the perforations. Near the bottom of the well, as much as 80% of the scale seems to have disappeared. Some redistribution of the scale materials may also have occurred since the post-treatment NORM curve is greater than the pretreatment NORM curve for two intervals below 1386 m. Therefore, the gamma ray spectroscopy data clearly indicate that this scale removal treatment was quite successful.

Pumping Procedures and Injection Results

The treatment schedule consisted of spotting 3.5 m^3 of a mixture consisting of 30% water and 70% $BaSO_4$ scale solvent into the workstring. Matrix rates and pressures were used to squeeze 3.0 m^3 of the mixture into the formation. The mixture was allowed to contact the $BaSO_4$ scale for 60 hours as previously determined by laboratory testing. A 5.0-m^3 15% HCl matrix acid treatment containing two gelled temporary bridging agent diverter stages followed the solvent soak. This sequence was consistent with what had been done in the past. The well was placed back on injection to evaluate the treatment.

The $BaSO_4$ scale dissolved across the perforations and near the wellbore, resulting in an injection rate of 221 m^3/day at 15,900 kPa wellhead pressure, far exceeding the target injection rate of 60 m^3/day.

The scale solvent was bullheaded and overdisplaced, leaving all the radioactive material downhole. The gas/oil ratio in the pool decreased to an acceptable level. An injection rate of 221 m^3/day using previous technology would have required an additional three wells. AFE costs per well are projected at $400,000 for a total economic value of $1.2 million. Additional savings may be realized as the treatment frequency is monitored. NORM scale handling and disposal costs are also eliminated. An injection rate profile from January, 1994 to June, 1995 is shown in Figure 3.

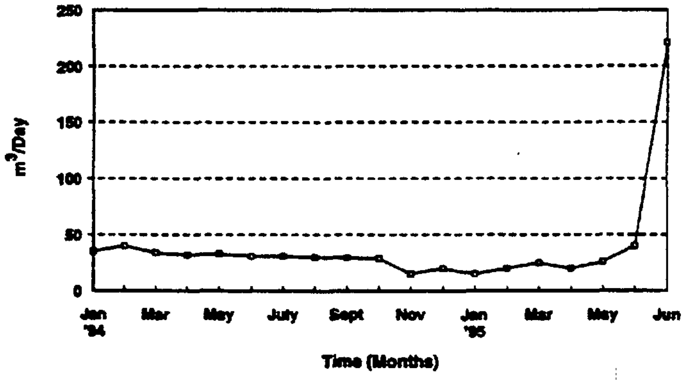

Fig. 3—Well injector summary.

Conclusions

- A scale solvent can be effectively used to remove NORM-contaminated $BaSO_4$ scale.
- The source of the scale and deposition tendencies were pinpointed through compositional water analysis.
- Scale identification and field laboratory data were used to specify the treatment schedule, including volumes and contact time.
- Pretreatment and post-treatment gamma ray spectroscopy logging data documented the effectiveness of scale removal.
- Operators now are able to mitigate NORM scale problems and can eliminate the costly disposal of these materials.

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Acknowledgments

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Technical Profile
of the
Envirocare of Utah, Inc.
NORM Disposal Operation

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Prepared for Presentation at
The API/GRI NORM Conference
NORM Management and Disposal Technical Session
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Technical Profile of the Envirocare of Utah NORM Disposal Operation

Envirocare of Utah, Inc. was issued its radioactive materials license in 1988 as the nation's first disposal facility for Naturally-Occurring Radioactive Material (NORM). The technical distinctions of the Envirocare operation are not widely known in the oil and gas production industry, and are key to evaluating the facility for potential NORM disposal needs. In addition, the Environmental Protection Agency is close to promulgating federal regulations for the control of NORM. These regulations may limit or eliminate NORM management by down-hole disposal, land-farming and dilution. The factors described below demonstrate that Envirocare is able to provide an alternative for the safe and practical removal of this significant Radium exposure source from the public, as well as providing necessary security for future corporate liability issues.

1) Naturally Suitable Site

The Envirocare site is the most suitable possible for radioactive materials disposal. The facility is located in the Great Basin West Desert approximately 80 miles west of Salt Lake City, Utah and 40 miles distant from the nearest population center. In 1976, the Department of Energy (DOE) began eight years of technical study at the site to demonstrate that its hydrogeologic qualities and isolated location would provide a safe burial place for such materials. 4.8 inches of annual precipitation, 60 inches of annual evaporation, less than 10% humidity, and deep, poor quality groundwater are some of the characteristics that make the site so safe. Based on the conclusions of eight years of

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federal study, a favorable Environmental Impact Statement was issued for the site in July 1984. Building on the DOE's work, Envirocare obtained its radioactive materials license in February 1988 for the nation's first NORM disposal facility. In almost two decades of activity at the site, there has never been a measurable release of radioactive materials.

2) License

Envirocare's license allows acceptance of materials contaminated with the standard oilfield isotopes of Radium-226 up to 2,000 pCi/g and Radium-228 up to 1,800 pCi/g. These limits are applicable to the maximum average activity in the waste and assume daughter products to be present in equilibrium. Soils, scale, tubulars, concrete, PPE, and other materials are all acceptable for disposal. In addition, waste materials do not necessarily need to be containerized for shipment, and can be delivered by truck, intermodal containers or railcars. This can provide significant packaging savings during remediation. The facility was designed and constructed for large volume operations and can accommodate shipping campaigns from 50 drums to 50,000 cubic yards.

All waste streams are carefully profiled and analyzed to ensure acceptability prior to shipment.

3) Cell Design

Envirocare does not employ trench-and-fill operations. The Envirocare disposal cells are constructed entirely above-grade and patterned after a DOE 1,000 year closure design. Over such long time periods, small void spaces in the embankment could

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compromise the integrity of even the most carefully engineered cell cap. For this reason all NORM wastes shipped to Envirocare are emptied from the container prior to disposal. Void spaces are eliminated through specific soil compaction and debris placement procedures. Materials are placed in 12" lifts and compacted to greater than 90% of Optimum Density. Compaction of every lift is tested at several locations using ASTM procedures before the next lift is placed. NORM materials from different generators are not commingled, and occupy an individual map location in the embankment.

Once a cell has reached its design height, a compacted clay radon barrier is constructed over the disposed materials. This barrier is seven feet thick and serves a dual purpose. First, the cap's design requires a permeability of less than 1×10^{-6} cm/sec for the lower six feet, and 5×10^{-7} cm/sec for the top 12 inches. This relatively impermeable barrier is also sloped, shedding precipitation off the cell. The Department of Energy has studied the effectiveness of engineered clay caps, concluding that >99% of infiltrating water is diverted off the embankment when properly designed caps are used. This study indicates that a facility utilizing a sloped, erosion-resistant cap in conjunction with a sorptive clay foundation provides a 10^{-4} dose reduction over standard trench-and-fill operations (DOE/LLW-207, Use of Engineered Soils and Other Site Modifications for LLRW Disposal). Also, designs utilizing natural materials combined with an arid site provide several orders of magnitude greater protection than concrete and other synthetic liner systems which decompose relatively quickly.

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In addition, as the name implies, the barrier prevents the radon gas from being released to the open air. The design retards radon migration within the clay matrix long enough for the gas to decay to a particulate (Rn-222 half-life @3.8 days). This is a significant consideration given that EPA's concern with radium stems largely from radon emanation. The radon barrier is protected from erosion and weathering through a series of aggregate filter zones and large diameter rock placed to a depth of 24 inches.

Importantly, this disposal method provides a high degree of control over the materials even several years after initial disposal. Unlike down-hole disposal, the disposal environment is easily accessed, monitored and its geotechnical properties are thoroughly characterized. In the unlikely event that contamination off-site does occur, it will be detected at a very early stage, and remedies are practical, proven and easily implemented.

Conclusion

Envirocare has safely accepted and disposed over 15 million cubic feet of NORM materials from dozens of public and private entities. The suitable natural qualities of the site combined with carefully engineered disposal cells will ensure the integrity of all materials disposed at Envirocare, safeguarding public health and safety as well as long-term corporate liability issues for generators.

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Modeling of NORM Injection in a Layered Geologic System

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Abstract

Subsurface injection and encapsulation of NORM contaminated materials were modeled to estimate contamination levels in a near-surface aquifer. By assuming instantaneous leaching of encapsulated materials, a conservative assumption, a single model was used for both disposal options.

A model was developed for injecting 100,000 barrels of 2,000 *pCi/L* NORM into a layered geologic system over a short period. The NORM was assumed to be released at depths from 300 to 10,000 feet below the ground surface. Subsequent transport of the radionuclides in the subsurface was simulated for a 100,000 year period. Radionuclide levels were monitored at receptors located 0.0, 0.2, 0.5, 1.0, 5.0, 10.0, and 20.0 miles down-gradient of the release bore. Depth of NORM release, regional groundwater gradient, receptor well pumping, and material conductivity were investigated to determine effects on measured radionuclide levels. This modeling effort found that even with conservative assumptions, calculated radionuclide levels were below those of regulatory concern at the receptor locations .

This study indicates that subsurface disposal of limited volumes of NORM contaminated waste, either by injection or encapsulation, constitute realistically safe methods for disposal. Modeling of actual sites using site-specific parameters, rather than conservative assumptions, should yield groundwater contaminant levels lower than those presented here.

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Introduction

The presence of naturally occurring radioactive materials (NORM) in oil and gas production and processing wastes has been recognized since the 1930's. However, concerns about the possible associated health risks did not arise until the mid-1980's when the industry and regulators realized that NORM occurrence was more widespread than originally thought and that activity levels could be quite high. Although it is widely acknowledged that both workers and the general public may be at risk of radiation exposure resulting from NORM contamination, the magnitude of that risk and the resultant need to regulate NORM have been debated. This study of subsurface disposal methods adds new information to the debate surrounding NORM regulation by modeling the physical processes of subsurface disposal and using this data to estimate activity levels in near-surface aquifers from various failure scenarios.

In the past few years, the petroleum industry has adopted methods for managing and disposing of NORM-contaminated wastes and equipment that are more restrictive than past practices and are likely to provide greater isolation of radioactivity. Currently acceptable subsurface NORM disposal methods include downhole encapsulation inside a plugged and abandoned well by license only, and underground injection into a subsurface formation by license only.

The scope of this study covers both downhole encapsulation and underground injection. Both activities were modeled using similar assumptions and settings. A three-dimensional model, SWIFT II (1), was employed to model casing failures that might occur at different depths during injection and the subsequent transport of radionuclides to downgradient receptor locations.

Underground injection was modeled by assuming a generic geologic setting of inter-layered sandstone and shale deposits. A conservative set of input parameters was used. Separate model runs were made assuming that during injection, a casing failure caused the entire volume of NORM-contaminated waste to be injected into each geologic layer in turn, including a drinking water aquifer. Radionuclide concentrations were calculated at a number of receptor locations in the drinking water aquifer ranging from 0 to 20 miles downgradient from the injection site. Additional calculations were made assuming two domestic wells pumping simultaneously at a rate of 14,400 gallons per day, 0.2 and 0.5 miles from the injection site, respectively. This rate was chosen as a reasonable rate for a domestic well in a sandstone aquifer.

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The estimates used to model underground injection were conservative for most parameters. The results suggest that deep underground injection of slurries with total volumes less than 100,000 barrels result in low activity levels in the groundwater (below the federal regulatory limit for radium in drinking water of 20 *p*Ci/L). Even injection directly into the drinking water aquifer does not result in appreciable concentrations of Ra-226 or Rn-222 at receptor locations as close as 0.2 miles away.

If instantaneous radium dissolution is assumed to be the leaching model, the model runs for underground injection effectively model downhole encapsulation as well. If more realistic leaching times are assumed, it can be predicted that radionuclide concentrations resulting from casing failures at downhole encapsulation sites will be lower at all receptor locations than those calculated for underground injection of the slurry.

Input parameters were carefully selected based on reviews of previous, related risk assessments; relevant published data; and discussions with other risk assessment researchers and representatives of federal and state regulatory agencies, industry, and academia. Sensitivity analyses of some of the key input parameters were conducted to assess their impact on predicted doses. Parameters chosen for the sensitivity analyses include those for which a set of definitive values could not be chosen due to variability in possible conditions (e.g., groundwater gradient or hydraulic conductivity) and those for which definitive data have not been collected but are thought to be quite variable (e.g., source term concentration or volume).

Description of Scenarios and Pathways

The subsurface disposal options investigated here are underground injection and downhole encapsulation. Underground injection is accomplished by injecting a slurry of NORM-contaminated wastes into a deep, subsurface formation. In this study, it was assumed that the injection zone was isolated vertically from a usable, groundwater aquifer by relatively impermeable, confining formations such as shales. Downhole encapsulation entails placing NORM-contaminated scale, sludge, tubing, and other small pieces of equipment (e.g., valves, filters, screens) inside the casing of a well that is to be plugged and abandoned. After the material is in place, the wellbore is sealed with cement or grout to isolate the contaminated material. It was assumed that the depth of encapsulation is similar to the depth of injection and that one or more confining units isolate that depth from the groundwater aquifer.

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To understand the risks associated with subsurface disposal options, radium concentrations resulting from the underground injection and downhole encapsulation of NORM-contaminated wastes were estimated at several different receptor locations. In addition, a number of possible casing failure scenarios also were simulated. Conservative assumptions were made in running the models, thereby resulting in higher calculated contaminant concentrations at the receptor locations than would be expected using more realistic parameters.

The simulated underground injection failure scenarios assumed casing failures in each of the geologic layers during the injection process. Each failure was assumed to release the entire volume of contaminated slurry into the geologic layer in which the failure occurred. Because it is unlikely that the entire volume of contaminated slurry would be injected before a casing failure was discovered, this assumption is conservative.

To model downhole encapsulation, it was assumed that the bore containing the encapsulated material was breached and that, upon failure, the radium dissolved instantaneously and moved horizontally into a geologic layer or vertically upwards along the wellbore and into a geologic layer. It was also assumed that the entire volume of contamination moved into a single geologic formation. By making these conservative assumptions, it was possible to use the model runs for underground injection to represent the failure scenarios for downhole encapsulation. If more realistic leaching times were used, it can be predicted that radionuclide concentrations in the surface aquifer resulting from casing failure would be lower at all receptor locations than those calculated for underground injection. Therefore, all scenarios simulated in this study are considered to represent both underground injection and downhole disposal activities and no distinction is made between these two options in the rest of this discussion.

For the general public, the exposure pathway related to subsurface disposal of NORM-contaminated wastes is groundwater contact or ingestion. In this study, it was assumed that the groundwater was extracted from a near surface aquifer by a pumping well located at various distances from the disposal well. Calculated activity levels were compared to drinking water standards.

Methods

A groundwater flow and contaminant transport model was used to model underground injection of NORM. The model assumed a generic geologic setting with conservative estimates of required parameters. For each scenario, radium concentrations were calculated at a number of

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receptor locations in a near surface aquifer. In addition, the sensitivity of the model to pumping wells, regional groundwater gradients, hydraulic conductivities, mesh size, and radium concentration levels was explored.

The SWIFT II model (1) was chosen for this assessment because it is three-dimensional, it calculates radionuclide transport with decay, and daughter products, and has been widely reviewed and validated. The SWIFT II code was originally developed to analyze coupled hydrologic, thermal, density, dual-porosity, and solute transport processes in porous media. Single-phase Darcy flow in the horizontal, vertical, or full three-dimensional space is evaluated by the finite-difference method. The code has capabilities for simulating continuous and discontinuous layers, time-dependent and constant sources and sinks, and both transient and steady-state groundwater flow. Under conditions of constant fluid density (dilute solutions), SWIFT II solves partial differential equations for hydraulic head and contaminant transport. These equations are coupled by the velocity term.

SWIFT II was configured to model the advective and dispersive transport of Ra-226 and its first daughter product, Rn-222, for each casing failure. The model, calculated radionuclide ratios in units of grams of Ra-226 per gram of fluid. These ratios of RA-226 were assumed to be the same as Ci/g concentrations.

Assumptions and Input Parameters

Geology

A series of inter-layered sandstone and shale formations were modeled as a generic site for subsurface disposal. This sequence is not representative of any particular area, but rather was used to obtain an understanding of the transport mechanisms that could effect NORM injection. The stratigraphy modeled consists of a top, 1,800-feet (ft) thick, sandstone layer considered to be the source of groundwater at the receptor locations, underlain by alternating shale and sandstone layers, each 1,600 ft thick. The total stratigraphic sequence consists of three sandstone and three shale layers. The layers were tilted with a slope of 0.01. The regional groundwater gradient was also assumed to be 0.01. This gradient is large, but gives conservative estimates for travel times and concentrations in the model.

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Properties

The sandstone hydraulic conductivity was assumed to be 1 x 10^{-2} feet per day (ft/day) and the shale hydraulic conductivity was assumed to be 1 x 10^{-6} ft/day (2). Porosity for the sandstone and the shale were assumed to be 0.2 and 0.1, respectively. Longitudinal (α_L) and transverse (α_T) dispersivities were set to 1,000 ft and 100 ft, respectively. These values are comparable to those suggested by Gelhar for sites of this size (i.e., 2 miles) (2).

The diffusion coefficients for both Ra-226 and Rn-22 were assumed to be 1.02 x 10^{-5} ft^2/day in sandstone and 2.29 x 10^{6} ft^2/day in shale. These coefficients are based on the diffusion of radium in pure water and modified to give an effective diffusion coefficient according to the equation (2):

$$\acute{D}_d = \left(\frac{n}{2-n}\right)^2 D_d$$

where D'_d is the effective diffusion coefficient, D is the diffusion coefficient in water at 25°C, and n is the porosity. The half-life for Ra-226 is 1,622 years and for Rn-222 is 3.825 days (3).

Dispersion was modeled as (2):

$$D_L = \alpha_L v + \acute{D}_d$$
$$D_T = \alpha_T v + \acute{D}_d$$

For these simulations, it was assumed that the radionuclide transport was not retarded, a conservative assumption.

Numerical Implementation

The conceptual site modeled was 10 miles (mi) wide, 22 mi long and 10,000 ft deep. The mesh used for the numerical simulation is shown in Figure 1. Because the model was symmetric about the *X* axis, only half the conceptual site was discretized in the numerical model. Through this use of symmetry, computational needs were reduced.

Both *X* boundaries were modeled as constant head boundaries with pressures equal to hydrostatic values. The *Y* and *Z* boundaries were modeled as no-flow boundaries. A groundwater gradient was induced by tilting the model to produce both a stratigraphic and groundwater slope of 0.01.

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The source location for the NORM injection was located on the *Y* = 1 boundary, to exploit symmetry, and approximately 2 mi from the *X* boundary. This location prevents the *X* boundary from influencing upgradient diffusion and transport of the radionuclides. The mesh is finer near the source as shown in Figure 1, giving better resolution in this area. This aides numerical stability and provides a more accurate solution.

Source Term

To calculate the source term, it was assumed that 100,000 barrels of NORM with a radium concentration of 2,000 pCi/L was injected over a period of four days. The total Ra-226 in this slurry was calculated to be approximately 7.0×10^{-5} pounds, injected at a rate of 0.875×10^{-5}lb/day. Again numerically, one-half the total amount was used because of model symmetry. In addition to the Ra-226 term, a 4.305×10^{6} lb/day water source term accounted for the 100,000 barrels of fluid injected. Again, it is one-half the total amount due to the symmetry of the model.

Casing Failure and Receptor Locations

Casing failures were simulated at three different depths within the top sandstone layer or aquifer: one shallow (300 ft), one at the mid-point (900 ft), and one near the bottom of the layer (1500 ft). Failures were simulated in the center of each of the underlying geologic layers, at depths of 2,600 ft (shale), 4,200 ft (sandstone), 5,800 ft (shale), 9,000 ft (sandstone), and 10,600 ft (shale). Casing failure was simulated by injecting the entire Ra-226 source amount over a four-day period at each node point. No attempt was made to determine the well types or pressures needed to obtain these injection rates. Thus, it was not determined if this injection scenario is feasible or even possible. Assuming this scenario is infeasible, feasible solutions would require a longer time period to inject the slurry, resulting in more dilution and more spreading of the plume, giving lower maximum concentrations calculated at the receptors. This assumption provides conservative estimates.

Receptor points were located 2.0 mi upgradient from the injection point (-2.0 mi), at the injection point (0.0 mi), and at points located 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0, and 20.0 mi downgradient of the injection site. All of the receptor points were located at a depth of 300 ft within the surface aquifer. Concentrations of both Ra-226 and Rn-222 were calculated at these sites over time. The upgradient receptor was used to evaluate the effects of diffusion in the model.

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The model was run first to calculate the Ra-226 and Rn-222 concentrations at each of the receptor points described above. Then the model was run to calculate these same concentrations at each of the receptor points, assuming that two pumping, municipal wells were located at the 0.2-mi and 0.5-mi receptor points. These wells were assumed to pump simultaneously at 14,400 gal/day for the entire 100,000-year time frame of the model. Table 1 identifies all of the receptor points modeled by distance from the injection well, failure scenario, and calculated concentrations of RA-226.

Results

Table 1 lists the concentrations of Ra-226 calculated at each receptor point for a number of failure scenarios. A worst-case scenario was simulated for each receptor point in which casing failure occurred at a depth of 300 ft in the surface aquifer, at the same depth as the receptor points. A more realistic, but still conservative, base case scenario was also simulated for each of the receptors in which casing failure occurred at a depth of 1500 ft, still within the near surface aquifer. The results of the worst-case and base-case scenarios are discussed below. Because all of the other failure scenarios (i.e., scenarios in which failure within or below the first shale layer) resulted in extremely low predicted concentrations (at least four orders of magnitude below the base case scenario concentrations) they are not discussed further in this paper.

The calculated Rn-222 concentrations for all scenarios were at least four orders of magnitude below those calculated for Ra-226. Because these concentrations are considered to be insignificant, they are not discussed in detail in this paper.

Due to the low calculated activity levels of RA-226, rather than computing dose or risk values, the calculated Ra-226 levels are compared to drinking water standards. As shown by Table 1, all scenarios, except a release at the same level as the receptor (0.2*p*Ci/g), result in levels lower than the drinking water standards of 20 *p*Ci/L .

Worst-Case Scenario

The worst-case scenario assumed that casing failure occurred at a depth of 300 ft. For this scenario, the maximum calculated concentration observed at the 0.2-mi receptor, was 1.3*p*Ci/g Ra-226, occurring approximately 700 years after failure. The model was unable to predict radionuclide concentrations at the receptor point located at the injection well (i.e., the 0.0-mi receptor) because the receptor point and the failure point were the same. (When the casing failure depth was set at 900 ft,

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just 300 ft below the receptor point, the maximum predicted concentration at the 0.0-mi receptor was 0.25 pCi/g Ra-226, approximately 500 years after failure.)

Base-Case Scenario

The base-case scenario for this study assumed a casing failure at a depth of 1500 ft, near the bottom of the surface aquifer. For this scenario, the model predicted a maximum concentration of 0.015 pCi/g Ra-226 at a depth of 300 ft at the site of the injection well (0.0 mi), approximately 1,800 years after failure. The maximum value calculated for this scenario, observed at the receptor located 0.2 mi downgradient, was 0.017 pCi/g Ra-226 occurring 3,600 years after failure. The predicted concentration at the 0.2-mi receptor is higher than the concentration predicted at the 0.0-mi receptor because contaminant transport occurs in a predominantly horizontal direction.

Sensitivity Analyses

Under the base case scenario, when pumping wells were located at the 0.2-mi and 0.5-mi receptor points, the model predicted a maximum concentration of 0.049 *pCi/g* Ra-226 at the 0.0-mi receptor, approximately 600 years after failure. The maximum values calculated at the pumping wells located at 0.2 and 0.5 mi were 0.002 *pCi/g* Ra-226, 600 years after failure and 0.012 *pCi/g* Ra-226, 1,800 years after failure, respectively. The effect of installing pumping wells at these two locations was to increase the vertical component of the contaminant migration, resulting in increased values at the 0.0-mi receptor, and to increase dispersion of the contaminant plume, resulting in lower values at the downgradient receptors. In addition, the installation of pumping wells decreased arrival times of the maximum concentration values at all receptors. The installed wells were pumped at a rate of 14,400 gal/day for the entire 100,000 year time frame of the simulation.

Sensitivity calculations were performed for regional groundwater gradient and hydraulic conductivity. Both were raised and lowered one order of magnitude above and below the assumed value used for the model. For these sensitivity calculations, only the base case scenario, failure at 1500 feet, was modeled.

Lowering the regional groundwater gradient or the hydraulic conductivity slightly lowered the calculated radionuclide concentrations at all of the receptors while increasing the arrival time. Raising the hydraulic conductivities of the sandstone and the shale by one order of magnitude, to 1 x 10^{-1} and 1 x 10^{5} feet/day, respectively, resulted in a

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maximum predicted concentration, observed at the 0.2-mi receptor, of 0.058 *p*Ci/g Ra-226, approximately 100 years after failure. Increasing the regional groundwater gradient to 0.1 resulted in a maximum concentration, observed at the 0.2-mi receptor, of 0.043 *p*Ci/g Ra-226, approximately 200 years after failure.

The sensitivity of the model to the mesh size used was also explored. The mesh spacing was reduced by a factor of two, resulting in a spacing of approximately 250 ft near the injection well. Using this mesh, the closest receptor beyond the 0.0-mi receptor was located at 0.1 mi downgradient. For this sensitivity analysis, two failure scenarios were considered: 1) the base-case scenario of failure in the surface aquifer at 1500 ft; and 2) the base-case scenario with the addition of two pumping wells located at 0.1 and 0.25 miles downgradient from the injection well, pumping at 14,400 gal/day. With the higher resolution mesh and the base case scenario, the model predicted maximum concentrations, observed at the 0.1-mi receptor, of 0.013 *p*Ci/g Ra-226. For the base case scenario with pumping wells, the model predicted maximum concentrations, observed at the 0.0-mi receptor, of 0.039 *p*Ci/g Ra-226.

The effect of higher contaminant concentration levels in the slurry was also investigated in the base-case scenario. If the contaminant concentration was increased from 2,000 *p*Ci/L to 4,000 *p*Ci/L Ra-226, the maximum concentration, observed at the 0.2-mi receptor, was 0.036 *p*Ci/g Ra-226, approximately 2,300 years after failure. This is approximately two times the calculated concentration for the base-case.

Conclusions

Predictably, the highest concentrations of Ra-226 calculated for the receptor points correspond to injection of the slurry directly into the drinking water aquifer. Using the assumed set of input parameters, in the worst-case scenario (i.e., casing failure at 300 ft), the maximum calculated concentration, observed at the 0.2-mi receptor point, was 1.3 *p*Ci/g Ra-226. When the failure point is lowered to a depth of 900 ft (still within the aquifer) and radium concentrations are calculated for a receptor point located at a depth of 300 ft directly above the failure point (i.e., the 0.0-mi receptor), the value is 0.25 *p*Ci/g Ra-226. Casing failure at a depth of 1,500 ft, still within the aquifer, resulted in a maximum concentration of 0.017 *p*Ci/g, well below drinking water standards of 0.2 *p*Ci/g.

All values calculated for injection into geologic units below the aquifer were at least five orders of magnitude below the highest observed

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value of 1.3 *pCi/g*. Calculated Rn-222 concentrations were insignificant, at least four orders of magnitude below those calculated for Ra-226.

Raising the hydraulic conductivities for the sandstones and shales by one order of magnitude increased the predicted Ra-226 concentrations slightly and lowered the arrival times of the maximum concentrations at the receptor points. Increasing the groundwater gradient by one order of magnitude had a similar effect. Reducing the mesh size by a factor of two had a negligible effect on the predicted results. Doubling the radium concentration level in the slurry effectively doubled the observed maximum concentrations at the receptors and had small effects on arrival times.

The assumptions made in modeling the subsurface disposal options are conservative for most input parameters. The results suggest that subsurface disposal of NORM-contaminated wastes in volumes less than 100,000 barrels result in very low levels of Ra-226 in the groundwater, well below the 20 *pCi/L* (0.2 *pCi/g*) regulatory limit for Ra-226 in drinking water. Using assumptions that more closely reflect realistic conditions would only result in lower predicted contaminant concentrations. The low levels of contamination calculated in this study indicate that health risks to the general public related to subsurface disposal of limited volumes of NORM are negligible.

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Table 1
Receptor Location Relative to the injection well (in miles).

Scenario	Receptor Location Relative to Disposal Bore (in miles) Values in pCi/g								
	0.0	0.2	0.5	1.0	2.0	5.0	10.0	15.0	20.0
Top Aquifer @ 300'	N/A	1.317	0.211	0.019	<<	<<	<<	<<	<<
Top Aquifer @ 900'	0.250	0.155	0.053	0.0082	<<	<<	<<	<<	<<
Top Aquifer @ 1500'	0.015	0.017	0.010	0.003	<<	<<	<<	<<	<<
1500' Low Conductivity	0.017	0.015	0.004	<<	<<	<<	<<	<<	<<
1500' High Conductivity	0.046	0.058	0.057	0.041	0.019	0.002	<<	<<	<<
1500' Low Gradient	0.011	0.011	0.005	<<	<<	<<	<<	<<	<<
1500' High Gradient	0.034	0.043	0.041	0.026	0.009	<<	<<	<<	<<
1500' Pumping	0.049	0.002	0.012	0.001	<<	<<	<<	<<	<<
1500' Fine Mesh	0.011	0.013 @ .1 miles	0.005 @.25 miles	<<	<<	<<	<<	<<	<<
1500' Fine Mesh w/ Pumping	0.039	0.020 @ .1 miles	0.001 @.25 miles	<<	<<	<<	<<	<<	<<
1500' 4,000 pCi/l	0.031	0.036	0.020	0.005	<<	<<	<<	<<	<<

[1] << indicates a calculated value below $1x10^{-5}$ pCi/g.

[2] All releases in layers below 1500 feet, (i.e. shale at 2,600 feet, sandstone at 4,200 feet, shale at 5,800 feet, and the lowest sandstone layer at 7,400 feet resulted in radium levels below $1x10^{-5}$ pCi/g.

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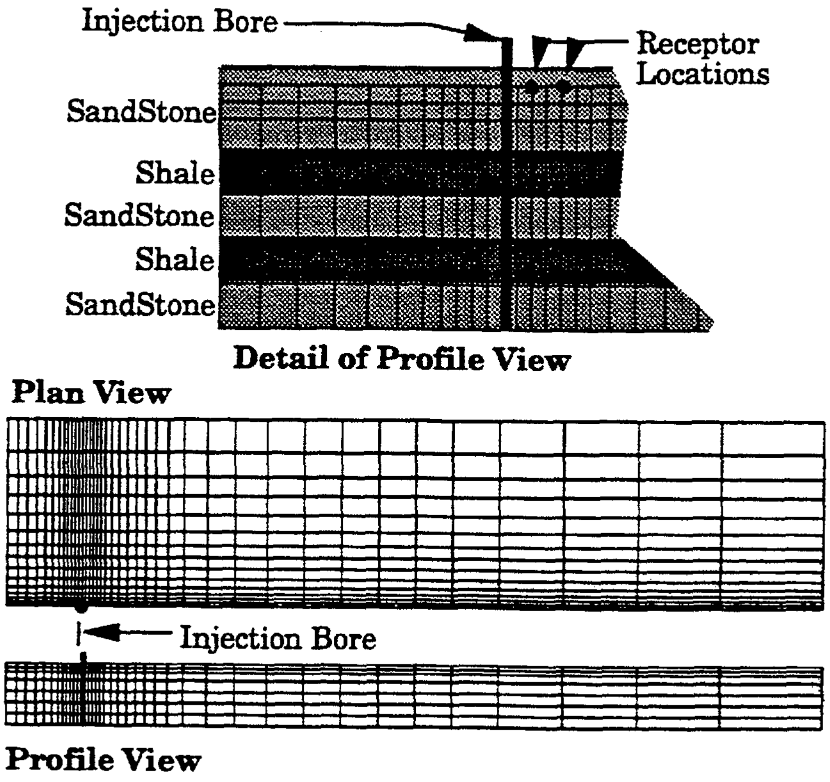

Figure 1 Mesh Used in the SWIFT II Model. Shown is the geologic layering, mesh discretization, injection bore, and examples of receptor locations.

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SESSION 4

NORM SCALE PREDICTION AND CONTROL

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Controlling Barium Sulfate Scale Deposition by Inhibitor Squeeze at the Guerra Well in South Texas: A Case Study

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Abstract

Formation of barium sulfate and calcium carbonate scale deposits in downhole tubing is a major problem for gas production in the Guerra well in South Texas. Prior to December 1993, mechanical removal of barite scales from production tubing was done on this well every twenty days. In late 1993, the Brine Chemistry Research Consortium, sponsored by the Gas Research Institute (GRI), at Rice University and Water Research Institute conducted a systematic laboratory and field study and an inhibitor squeeze treatment was recommended. The well was squeezed with bis-hexamethylene triamine tetramethylene phosphonic acid (BHTMP) in December 1993. After the squeeze, the barium sulfate scale problem was eliminated, but the well still produced light calcium carbonate scale in the production tubing near the perforations and required minimal chipping every three months. The well continues to produce since the squeeze treatment and has been monitored continually. By squeeze treatment, the operator's estimation of over $80,000/yr savings has been realized. An integrated study is presented in this paper, including analysis of brine samples, scale prediction, laboratory evaluation of inhibitors, simulation of inhibitor squeeze, long-term monitoring of field inhibitor return and brine chemistry.

Keywords: Barium sulfate, calcium carbonate, NORM scales, scale inhibitors, Squeeze treatment

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Introduction

The Guerra well, located in South Texas, produces 8.5 MMSCFD natural gas, 50 BO/D, and 120 BW/D. The reservoir of the gas well is relatively deep (at approximately 14,000 ft). The bottom hole temperature is typically about 340°F and the reservoir pressure is about 6997 psi. The reservoir formation is composed of calcite (20 to 40%), quartz (25 to 30%), feldspar (20%), and clay minerals (10 to 35%). Among the clay minerals, illite is typically 80% and chlorite is about 20%. The porosity is about 18%. The permeability varies from 0.01 to 0.05 mDarcy and it is a fracture-stimulated reservoir. The content of carbon dioxide in the gas phase is about 0.5%.

Prior to December 1993, two types of water-formed scale deposits, barium sulfate and calcium carbonate, were encountered in the production system (mainly in downhole tubing). Hard scale deposits of barium sulfate pose a severe operational problem to production operation since they can not be easily removed once deposited and are often associated with naturally-occurring radioactive materials (NORM) (1). Before the squeeze treatment, discussed in this paper, barium sulfate and calcium carbonate scales had to be removed by chipping. The annual cost is estimated to be $87,000 for broaching and chipping.

Sponsored by GRI, the Brine Chemistry Consortium at Rice University and Water Research Institute conducted an integrated study of the scaling condition of the well and designed a treatment plan to control barium sulfate scaling. This paper summarizes the laboratory design and field implementation of inhibitor squeeze treatments in the Guerra well. First, brine analysis and scaling tendency are described. Next, laboratory tests of scale inhibitors are presented. Finally, the field squeeze and results are shown.

Brine Chemistry and Scaling Tendency

Brine samples were taken from the gas well in the well head and analyzed in the laboratory. The chemical composition of the brine and other information concerning the well are listed in Table 1. The chemical analysis is performed at room temperature and pressure. The concentration of cations was analyzed using inductively coupled plasma spectrometry, while the chloride and carbonate alkalinity were determined by titration. The concentration of sulfate was determined by turbidimetric method and found to be very small (< 5 mg/l).

The scaling tendency of the brine in terms of saturation index (SI) under various production conditions was calculated based on EQPITZER program (2) which is a computer program for speciation and calculation of saturation index of brines with respect to common water-formed scale deposits, such as calcite, gypsum, anhydrite, celestite, and barite, based on Pitzer equations. The saturation index is defined as the logarithm of the ratio of the ionic activity product over the thermodynamic solubility product.

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Table 1. Chemical composition of the Guerra brine.

Species	Concentrations (mg/l)	(mmol/l)
Na^+	19871.8	864.4
Mg^{2+}	54.0	2.2
Ca^{2+}	6500.0	162.2
Sr^{2+}	700.0	8.0
Ba^{2+}	550.0	4.0
Fe (total)	12.0	0.2
Cl^-	43000.0	1228.6
SO_4^{2-}	<5.0	<0.052
Ac (HCO_3^-)	281.0	4.6
IS (M)		1.42
pH (meas.) at Surface		7.10
$CO_{2(g)}$ in the gas phase		0.5 %

The saturation index calculated is presented in Table 2. It can be concluded that serious scaling of calcium carbonate will occur (SI greater than 1) when the reservoir pressure drops, which is proven by the occurrence of calcium carbonate scales in the tubing near the perforations where pressure drops greatly. In the case of barium sulfate, decrease of pressure to atmospheric pressure only creates an SI of 0.03 (near equilibrium), but the cooling of brines can produce scales of barium sulfate (SI up to 1.2 if the brine was cooled down to room temperature). Clearly, the analysis or the interpretation made needs further work.

Table 2. Calculated saturation index (SI) for the Guerra brine with respect to common water-formed scale deposits.

Parameters	Locations			
	Tubing	Well Head	Surface	
T (°F)	236	236	236	77
P (psi)	6997	397	14.7	14.7
pH (calc)	5.34	6.71	7.94	7.91
SI (calcite)	-0.27	1.21	2.24	1.94
SI (barite)	-0.23	0.01	0.03	1.17
SI (celestite)	-1.60	-1.37	-1.35	-1.70
SI (anhydrite)	-2.05	-1.75	-1.72	-2.70

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Inhibitor Evaluation and Squeeze Simulation

A series of commercially available scale inhibitors were tested in the laboratory for their efficiency against the scaling of barium sulfate. Both static and dynamic tests were conducted.

The static testing of inhibitor efficiency was based on the measurement of the nucleation induction period of barium sulfate in the presence of inhibitors (3), that is, the relative prolongation of nucleation induction period in the presence of different scale inhibitors at the same concentration in mg/l. The static test results in the ranking of scale inhibitors according to their efficiency in delaying the nucleation.

The dynamic testing of scale inhibitor was performed in a high-temperature and high-pressure flow-through apparatus which simulates the production system in the laboratory (4). The dynamic test results in an effectiveness ranking of the scale inhibitors by the minimal effective dose for each inhibitor.

Common commercial scale inhibitors have been tested. These inhibitors include 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP), nitrilotrimethylene phosphonic acid (NTMP), hexamethylene diamine tetramethylene phosphonic acid (HDTMP), diethylene triamine pentamethylene phosphonic acid (DTPMP), bis-hexamethylene triamine tetramethylene phosphonic acid (BHTMP), polyacrylates (PAA, molecular weight from 1000 to 7000), phosphinopolycarboxylates (PPPC, molecular weight from 1900 to 3800), and sulfonated polyacrylic acid (SPA, molecular weight of 3500). Based on both tests, BHTMP was found to be effective and superior to other scale inhibitors and thus recommended for squeeze treatment use.

Simulation of the squeeze process was made in the laboratory in order to obtain information concerning the retention and release of the inhibitor BHTMP into and from the Guerra core material. The inhibitor BHTMP was pumped into a packed column consisting of synthetic materials with similar mineralogical composition as the formation rock and was shut in for two days. Then, the column was turned around and a synthetic brine was pumped through the column from the opposite direction, to simulate injection and return flow. The concentration of BHTMP was continuously monitored for over 60 pore volumes. The flow rate was 10 ml/min. The results of inhibitor return are presented in Fig. 1.

Two sets of simulation were performed, using two different injection concentrations (5% and 0.5% BHTMP). The inhibitor concentration remains over 1 mg/l for over 100 pore volumes (Fig. 1A) and the percentage of inhibitors returned is less than 30% (Fig. 1B).

Inhibitor Squeeze Design

Based on information from the laboratory evaluation of inhibitors and column simulation of inhibitor squeeze under simulated field conditions, a chemical inhibitor squeeze treatment was designed and recommended for the Guerra gas well. The squeeze formula includes five phases, which are listed in Table 3.

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Table 3. Design and recommendation of an inhibitor squeeze treatment.

Phase	Process	Volume (bbl)	Additives	
			Composition	Concentration
1	(Preflush)*	25	HCl	0.5%
2	Pill	270	BHTMP	3537 mg/l
3	Overflush	250	Filtered field brine	
4	Shut-in	48 hours		
5	Production			

* For this squeeze no acid preflush was used, because acid had been used two days earlier to aid in removing existing scale. Normally, an acid preflush would be recommended.

The preflush solution (0.5% hydrochloric acid with a corrosion inhibitor) was used for cleaning the production tubing by removing calcium carbonate scale deposits. The squeeze pill consists of the inhibitor (bis-hexamethylene triamine tetramethylene phosphonic acid, BHTMP in acid form) in the filtered produced water. The overflush was used to push the inhibitor pill further into the reservoir formation and the shut-in period of two days was necessary for the fixation of the inhibitor into the formation rock through the reaction of inhibitor acid with the formation rock.

Inhibitor Return and Economic Impact

The inhibitor squeeze was done on December 21, 1993. After the two-day shut-in, the well was back into production on December 23. Long-term monitoring of the inhibitor return has been performed since the squeeze.

The concentration of the inhibitor returned as a function of the volume of brines produced cumulatively since the squeeze is presented in Fig. 2. The inhibitor concentration remained above 1 mg/l for the initial 20,000 bbl of brine produced (approximately 167 days) and maintained around 0.5 mg/l for over 50,000 bbl of brine produced (about 417 days) (Fig. 2A). The amount of inhibitor returned, as of this writing (15 months), is less than 20% of the total amount of the inhibitor squeezed (Fig. 2B).

After the squeeze, the Guerra well produced gas and oil with few problems due to scale formation for about 18 months. During this period, the well was periodically tested for downhole scale. Recently, the gas production fell off due to blockage by scale formation. Scale samples were obtained and found to be barium sulfate. A new squeeze treatment is planned, which includes a mixed inhibitor treatment for both calcium carbonate and barium sulfate.

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The cost savings for the chemical squeeze are estimated by the operator to be $78,500 per year. In addition, 24 days of more production per year has been realized.

Summary

The scaling problem of barium sulfate in downhole tubing in the Guerra gas well in South Texas was eliminated by inhibitor squeeze with bis-hexamethylene triamine tetramethylene phosphonic acid (BHTMP). The squeeze has lasted for 18 months. Cost savings are estimated to be more than $80,000 per year by the operator. However, light scaling of calcium carbonate still extists and chipping is required every 90 days. The following conclusions can be drawed from this case study:

1) BHTMP is an efficient inhibitor for the inhibition of barium sulfate scaling, especially in high calcium brines.

2) Inhibitor squeeze treatment is an effective and economic method for controlling scale deposition in downhole conditions in the gas/oil production system.

3) In the inhibitor squeeze treatment, blends of inhibitors may be needed instead of a single inhibitor to control the formation of mixed minerals, such as barium sulfate and calcium carbonate. Such combinations are presently being tested.

ACKNOWLEDGEMENTS

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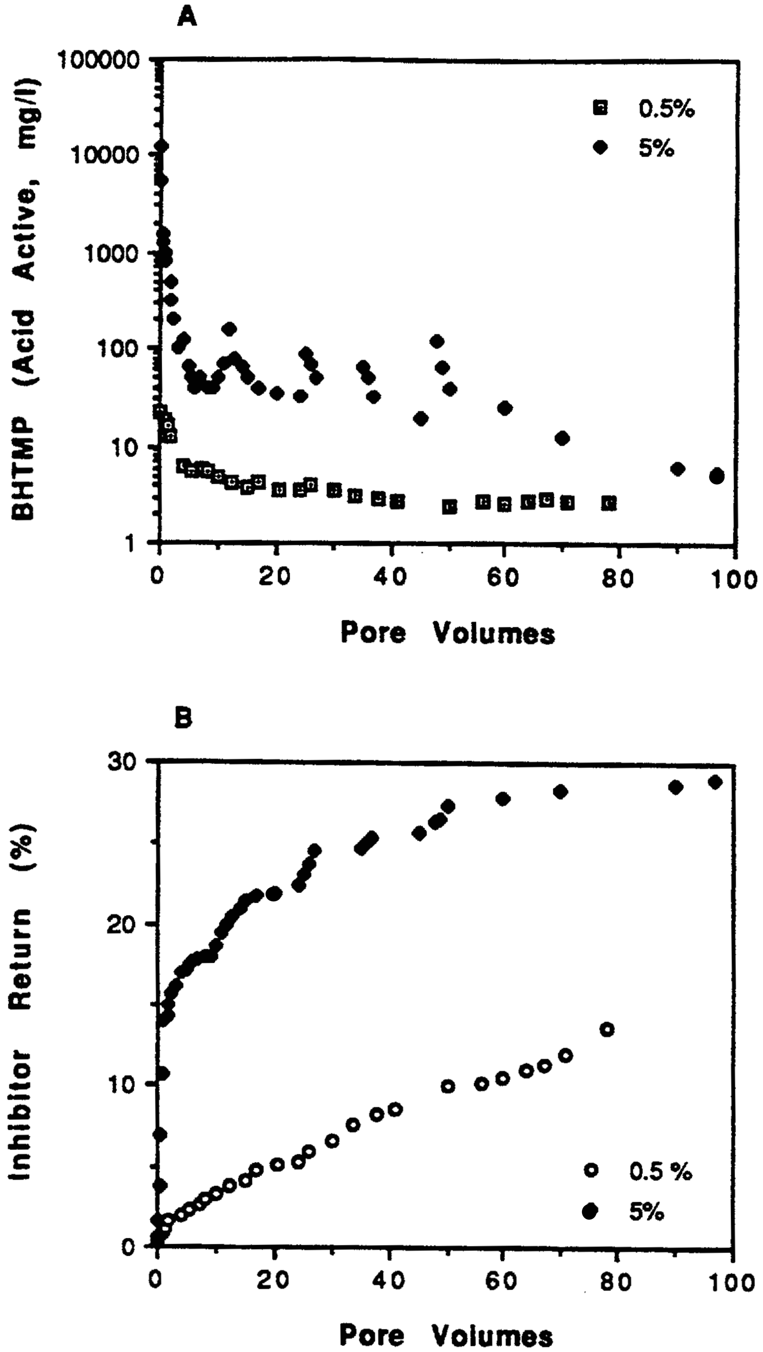

Figure 1. The squeeze simulation result of BHTMP in synthetic core materials. The open circles represents data from squeezing 0.5% inhibitor acid, while the solid diamonds represent data from squeezing 5.0% inhibitor acid.
A: the return concentration of the inhibitor.
B: the inhibitor return percentage.

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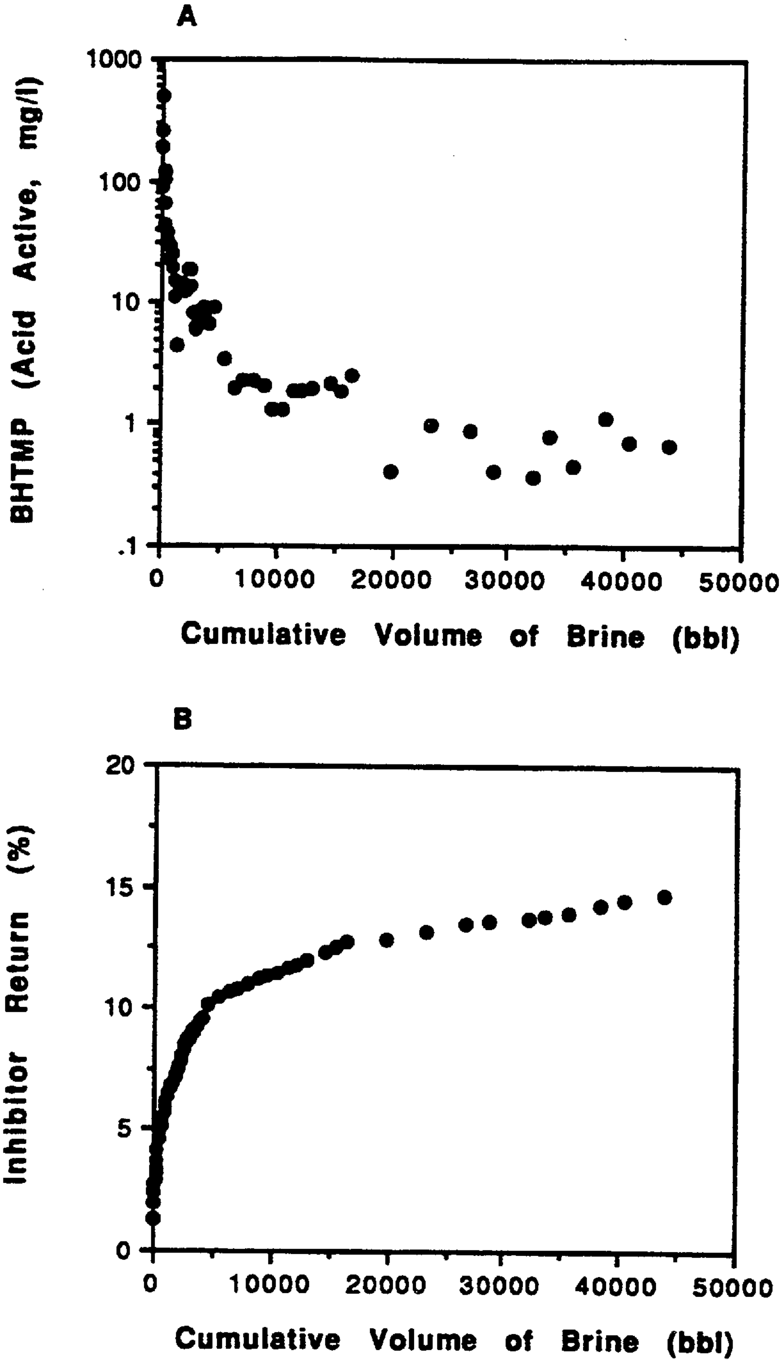

Figure 2. The return of inhibitor BHTMP as a function brine flow back in the Guerra well after the squeeze.
A: The concentration of BHMTP in flowback brines.
B: The percentage of BHTMP in flowback brines.

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A Laboratory and Field Study of the Mitigation of NORM Scale in the Gulf Coast Region of the United States

Dr. John E. Oddo, Dr. Xiliang (Steve) Zhou, Water Research Institute, Inc., Mr. Jorge Gamez, Gas Research Institute, Dr. Shiliang He, Professor Mason B. Tomson, Rice University

ABSTRACT

Some oil field scales have the potential to contain regulated levels of naturally occurring radioactive materials (NORM). The most common NORM containing scale is $BaSO_4$, or barite. This paper presents the results of a Gas Research Institute sponsored study that investigates the causes of NORM scale formation and mitigation techniques employed in the field.

Chemical threshold scale inhibitors are generally employed to inhibit scale formation in production systems. Laboratory work using a GRI patented inhibitor evaluation apparatus has produced results that can be used to determine the most effective inhibitor for a specific field application. The matrix of ionic strength and temperatures and the most effective inhibitors are discussed in the paper. In addition, a new method to evaluate inhibitors has been determined which is based on the delayed nucleation times of scale crystals in the presence of scale inhibitors. This method is faster than flow through (tube blocking) inhibitor evaluations and has been found to correlate well with flow through results. Although flow through testing is still recommended for definitive evaluations, the new method is recommended as a screening procedure.

Two NORM fields have been studied in the Gulf Coast Region. In these fields, three causes of NORM scale have been identified. Treatment procedures can vary depending on the type of NORM scale encountered to realize optimum results. Field treatment techniques employed in the two fields studied are summarized in the paper.

Inhibitor squeeze procedures have been studied in the laboratory and in the field. A squeeze simulation apparatus was constructed to research inhibitor squeeze practices in the laboratory. Results from this work resulted in successful inhibitor squeeze applications in the field. The inhibitor squeeze apparatus and the field results are discussed in the paper. Squeeze life has been extended from an average of two to six months to two to three years or more as a result of this work.

INTRODUCTION

Mineral scales are deposits produced in field production facilities due to temperature and pressure changes or commingling processes during the gas and oil recovery processes. Scale deposition in producing wells and associated facilities negatively impacts rates of production and is expensive to treat and remediate, regardless of the environmental regulations involved. The most common NORM containing scale is barium sulfate, or barite.[1, 2, 3] Although the radionuclides responsible for NORM in barium sulfate scales are radium-226 and radium-228, these radionuclides do not precipitate directly, but are co-precipitated in the barium sulfate scale causing the scale to be radioactive as in the following equation:

$$Ba^{2+} + Ra^{2+} + SO_4^{2-} \Rightarrow Ba(Ra)SO_4\ _{\text{(barite solid)}}$$

The concentration of radium in the barite solid is always far less than the concentration of barium.

The concentration of radium in the flowing brine is generally not high enough to be regulated, but when concentrated in scale deposits radiation levels can be in excess of regulated limits. Unlike most other common scales, no easy economic method exists to chemically remove barium sulfate from field equipment. Furthermore, the scale often forms near or at the bottom of a well. The scale is usually removed by mechanical means. This results in lost production, damaged or ruined equipment and downtime. In addition, the recovery of solid NORM scale materials leads to storage problems of the regulated material. Barium sulfate scale occurs during gas and oil production in many places throughout the world and in the United States including the Michigan Basin, the Gulf Coast, Oklahoma and Alaska to name a few.

Though radium in scale decays to radon gas, there is no build-up of radon in conjunction with NORM scales due to the 1620 year half-life of radium-228 combined with the relatively short time since the scale formation.

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LABORATORY RESULTS

Chemical scale inhibitors are commonly used to prevent or inhibit scale formation in production systems.[4, 5] These chemicals inhibit crystal growth and are generally effective at less than 10 - 20 mg/l in the produced water. It is extremely important to evaluate scale inhibitors for field use under conditions similar to those that will be encountered in the field. Inhibitor performance is dependent on temperature, overall water chemistry and the ratio of barium to sulfate in the case of barium sulfate scale. An inhibitor that performs well under a certain set of circumstances may not perform as expected under a different set of conditions. It is important to find the most effective inhibitors to use before weighing secondary issues such as cost per pound.

An inhibitor squeeze is performed by pushing scale inhibitor into a producing formation and fixing the inhibitor in the formation. When the well is flowing, inhibitor is produced along with the formation water. Evaluating inhibitors is even more important with respect to a squeeze since the life of the squeeze may be determined by the effectiveness of the inhibitor. That is, if two inhibitors return at the same concentration with one being effective and the other not, the well with the less effective scale inhibitor will need to be treated much more often. This difference can be weeks or months instead of years of successful inhibitor performance from one squeeze.

Inhibitors were evaluated in the laboratory using a dynamic flow-through simulation system. A GRI patent is pending on the inhibitor evaluation apparatus.[6] Scale inhibitors should not be evaluated using so-called open beaker tests. These tests yield inaccurate and often costly results due to inherent problems associated with the technique.[7]

Previous work suggested that the phosphinopolycarboxylate-29 scale inhibitor was most effective for barium scale inhibition.[8, 9] However, this inhibitor is known to be incompatible with many medium - high calcium brines. Further tests have been performed using simulated brines of varying water chemistries at different temperatures to identify scale inhibitors that will perform well under these varying conditions. Although this work is in progress, available results suggest other inhibitors are more effective under different conditions. Inhibitors have been evaluated using the water chemistries outlined in Table 1. Results of the evaluations are shown in Table 2. The results of the inhibitor evaluations are presented as the minimum effective dose (MED) to inhibit scale under the conditions of the evaluations. During the dynamic tests, scale must be 100% inhibited, therefore, percent inhibition is not applicable. Concentrations are "as product" of the concentrated material that is normally obtained from the manufacturer. None of the products were neutralized or diluted before the evaluations.

Although much more testing remains to be done for the inhibitors and for other inhibitors not shown, some conclusions can be drawn from the data. BHMDTMP (bishexamethylenediaminetetra (methylene phosphonic) acid and BHMTPMP (bishexamethylenetriamine-penta(methylene phosphonic) acid may have applications over a wide range of conditions.

The phosphonate evaluated at 75° F does not perform well. This is consistent with the observations of others, and with results from our own laboratory that phosphonates are not as effective at temperatures below approximately 120° F. Note the effectiveness of the PPPC-29 material in the 0.5 M ionic strength water consistent with previously reported results.[9] The overall results of these evaluations are also consistent with the results of He.[10, 11] At lower temperatures, phosphate esters[8] and tripolyphosphate (He, Personal Communication) are also effective and may have cost advantages.

FIELD RESULTS

Over one hundred and eighty water samples have been obtained from wells and facilities in the Gulf Coast region. These waters have been analyzed for scale forming components including barium and sulfate. The scale forming tendencies of the produced waters were determined using saturation index equations developed by the authors.[12] NORM scale in the Gulf Coast region has three primary mechanisms of formation:

1) A high saturation index and resultant scale formation can also be generated simply by the temperature and pressure changes exerted on a reservoir water that is at equilibrium with barium sulfate at reservoir conditions.
2) Scale can form due to the introduction of sulfate into a reservoir containing barium by seawater flooding and;
3) NORM scale can also form by the commingling of waters from different zones or wells where one zone is relatively high in barium and the other relatively high in sulfate.

All three of these causative factors have been observed in the field and are discussed below.

Field A - Offshore Gulf of Mexico

Field A is an offshore gas and oil field in the Gulf of Mexico. The field has been seawater flooded to maintain production levels. Produced water and hydrocarbons are piped onshore for processing. Production data, radiation readings and water samples were collected in the field on several occasions.[13] Sixty-seven water samples from wells and surface facilities were obtained from this field. Only one wellhead was identified as concentrating NORM in scale. In addition, only one of the surface facilities was found to be contaminated with NORM. Water transfer pipes and vessels beyond the individual platform sites are contaminated with NORM scale. The scale has been identified as barium sulfate by x-ray spectroscopy.

The produced waters from the wells are typically characterized by being either relatively high in barium or

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sulfate, although some wells are relatively equal in their barium and sulfate concentrations. Barium sulfate scale is predicted[12] in the well where NORM readings above background were detected and in two surface facilities. However, barium sulfate scale was not predicted nor found in any of the other wells. Figure 1 shows the sulfate vs. chloride concentrations of the produced waters. The dramatic increase in the sulfate concentrations near 20,000 mg/l chloride demonstrates the seawater breakthrough in these wells. (Seawater sulfate and chloride concentrations are about 2700 mg/l and 19,375 mg/l, respectively.) The higher sulfate concentrations noted at about 95,000 mg/l chloride are due to production from a high sulfate low barium zone. Figure 2 is a plot of the barium vs. sulfate concentrations of the waters of Field A showing that an increase in one variable essentially drives the other variable to a very low or non-detectable level due to the low solubility of barium sulfate. Unlike other barium sulfate scaling locations, such as the North Sea, barium sulfate scale in this field does not form in the production wells as a result of past seawater flooding. This may be a result of the much smaller flow rates encountered in the field (≅ 500 - 1000 BFPD).

The primary causative factor for the formation of NORM scale in Field A is the commingling of waters at the surface from the different wells and platforms in the field. The produced water is transported on-shore in pipelines and these pipelines are the most contaminated with NORM scale. The pipeline begins at the furthest point from shore and continues toward shore with the highest NORM scale readings being in the pipeline just after the facility closest to shore. Scale does not form in the wells from the past seawater flooding nor as a result of changes in temperature and pressures associated with production (except for one well).

Current plans for this field involve surface treatment with a phosphate ester scale inhibitor. This is reasonable based on the lower cost of phosphate esters, as opposed to phosphonates, and the relatively low temperatures encountered in the subsea flowlines. Phosphate esters have been found to be effective barium sulfate scale inhibitors in previous studies[8], as well as by others.

Based on the study of this field and others, the commingling of waters from different wells or zones, with or without seawater flooding is the prevalent cause of NORM scale deposition in the Gulf Coast. Incipient scale in a well as a result of production changes in temperature and pressure may be less prevalent, but does occur as in Field B below.

Field B - Atchafalaya River Marsh Area

Field B is an example of wells that produce scale in the well tubulars and in the surface facilities due only to the temperature and pressure changes associated with production. The field has been visited several times to collect water samples and radiation data.[13] NORM scale has been found in the wellheads, the production tubulars and in the surface facilities. The NORM scale has been identified as barium sulfate. All of the wells will scale NORM materials if the temperature is cool enough. (The solubility of barium sulfate decreases as the temperature decreases, unlike calcium carbonate.[12])

The wells produce into flowlines that carry fluids to central facilities where the hydrocarbons are separated from the water. The waters are then commingled and injected into a disposal well. No NORM materials have been identified in the disposal well system.

Several wells are predicted to form calcium carbonate scale. These wells which scale calcium carbonate generally do not scale extensively with barium sulfate at the wellhead. However, these wells will scale barium sulfate and will precipitate specifically at chokes and bends or any points of turbulence. In addition, these wells may scale barium sulfate downhole at points of turbulence, such as, gas lift valves. Although some wells may be supersaturated with calcium carbonate at the wellhead, it should be noted that calcium carbonate may be undersaturated or only slightly scaling in some wells downhole due to the increased downhole pressure and may therefore scale barium sulfate. The tubing was pulled in a treated well for replacement due to corrosion failure. Figure 3 is a plot of the radiation counts of the pulled tubing vs. depth in the well. The dark diamonds on the figure are the locations of the gas lift valves in the well. The gas lift valves were notably scaled upon inspection. It can be observed from Figure 3 that the turbulence caused by the gas lift valves was the cause of the barium sulfate NORM scale deposition.

All of the wells in this field except for the pulled well are being treated with a combination scale inhibitor to prevent the deposition of calcium carbonate scale at high temperature and barium sulfate scales at relatively lower temperatures. The scale inhibitor is being injected into the gas lift systems of the wells until a decision is made to squeeze the wells with scale inhibitor. The two inhibitors being used are ATMP (aminotrimethylene phosphonic acid) and BHMDTMP (bishexamethylene-triaminetetra(methylene phosphonic) acid). This procedure has inhibited scale above the lowest gas lift valve, although there is still some scale deposition below the gas lift valves in two of the wells. The pulled well was squeezed in late 1994 to prevent future scale deposition. The tubing was pulled again on March 20, 1995 and was found to be scale free. However, due to unrelated production problems, the well was completed in a different zone. This new zone may be squeezed depending on the water analyses and the scaling tendency of the new zone. Water samples have been collected from this zone.

The squeeze parameters used were:

Pre-flush - 15 barrels of produced water with surfactant and sodium bisulfite.

Inhibitor Pill - 80 barrels of 1.6% ATMP for calcium carbonate inhibition and 1.6% BHMDTMP for barium sulfate inhibition in produced water with sodium bisulfite.

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Overflush - 147 barrels of produced water with sodium bisulfite.

This squeeze is expected to last two - three years, but the influence of the turbulence caused by the gas lift valves makes this somewhat uncertain.

CONCLUSIONS

1. Barium sulfate scale inhibitors vary dramatically in performance depending on temperature, water chemistry and barium:sulfate ratios.
2. Preliminary work indicates that at lower temperatures (below about 120° F), phosphate esters and polycarboxylates may be more effective than phosphonate scale inhibitors for barium sulfate.
3. At higher temperatures, BHMDTMP and BHMTPMP appear to have a wide range of application and are more effective than other scale inhibitor, both in terms of cost and performance.
4. Three causes of NORM scale deposition have been identified in the Gulf Coast Region:
   1) A high saturation index and resultant scale formation can also be generated simply by the temperature and pressure changes exerted on a reservoir water that is at equilibrium with barium sulfate at reservoir conditions.
   2) Scale can form due to the introduction of sulfate into a reservoir containing barium by seawater flooding and;
   3) NORM scale can also form by the commingling of waters from different zones or wells where one zone is relatively high in barium and the other relatively high in sulfate.
5. The most prevalent cause of NORM scale formation is the commingling of produced waters from different wells or production zones, with or without seawater flooding.
6. Based on the work, scale in the production tubing due to past seawater flooding may not be as severe a problem in the Gulf Coast as in other areas, e.g., the North Sea.
7. Incipient scale occurring in a well due to the temperature/pressure changes exerted on the reservoir brine during produced water may not be as prevalent, but does occur.
8. NORM scale deposition can be inhibited in the field with scale inhibitors currently available. However, it is essential to perform scale inhibitor evaluations to find the most effective scale inhibitor at conditions similar to those encountered in the field.

ACKNOWLEDGEMENTS

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Table 1. The chemistries of the four waters used in the chemical inhibitor evaluations. This work is in progress, and more inhibitors are being evaluated. This work should not be interpreted as presenting the most effective known inhibitors at the indicated conditions.

		Concentration (mg/l where applicable)		
Water	A	B	C	D
Component				
Ba	200	135,175,220,260*	225,320,420,500	275,385,500,615
Ca	7000	518	1500	3000
Mg	1000	400	500	500
HCO_3	25	88	88	100
Cl	135000	15880	51000	85000
SO_4	250	135,175,220,260	225,320,420,500	275,385,500,615
Ionic Strength (M)	4.03	0.5	1.5	2.5
TDS	221000	27000	84000	140000

* Inhibitors are being evaluated at four different temperatures with a constant saturation index of 2.3. Therefore, the concentrations of barium and sulfate had to be increased at each temperature to maintain a constant supersaturation due to the increased solubility. The pressure is 150 psi.

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Table 2. The minimum effective dose (MED) of scale inhibitor required to inhibit scale under the designated conditions. This work is in progress, and more inhibitors are being evaluated. This work should not be interpreted as presenting the most effective known inhibitors at the indicated conditions. All MED concentrations are as product.

	Concentration (mg/l)			
Water **Inhibitor**	**A**	**B**	**C**	**D**
Temperature 75 F				
BHMDTMP		0.8	0.5	1.5
PPPC-29		1.0	0.5	0.5
PPPC-30		1.0	0.8	0.5
Phosphate Ester		0.5	0.5	2.3
DTPMP		1.0	1.0	2.0
BHMTPMP		0.5	0.5	0.8
DETHMP		0.5	0.5	2.3
Temperature 125 F				
BHMDTMP		0.5	0.5	0.5
PPPC-29		0.5	1.3	2.5
PPPC-30		1.0	1.8	4.0
Phosphate Ester		1.5	0.5	2.5
DTPMP		0.5	1.3	5.5
BHMTPMP		0.5	0.5	0.7
DETHMP		0.5	0.5	3.5
Temperature 175 F				
BHMDTMP		0.8	1.0	5.5
PPPC-29		1.8	1.5	>25
PPPC-30		2.3	2.5	22.5
Phosphate Ester		1.0	1.3	10.5
DTPMP		3.5	1.5	>25
BHMTPMP		0.8	0.8	2.5
DETHMP		1.0	2	12
Temperature 225 F				
BHMDTMP	3.2	0.5	5	20
ATMP	8.8			
PPPC-29	>20*	18	>25	>25
PPPC-30		3.5	24.5	>25
Phosphate Ester		1.5	15	19
DTPMP		10	>25	>25
BHMTPMP		0.5	4	15
DETHMP		15	>25	>25

* Incompatible with the brine before inhibition.

BHMDTMP - bishexamethylenediaminetetra(methylene phosphonic) acid; PPPC-29 - phosphino-polycarboxylate-29; PPPC-30 - phosphinopolycarboxylate-30; DTPMP - diethylenetriaminepenta-(methylene phosphonic) acid; BHMTPMP - bishexamethylenetriaminepenta(methylene phosphonic) acid; DETHMP - dipropIethylenetetraaminehexa(methylene phosphonic) acid; ATMP - aminotrimethylene phosphonic acid.

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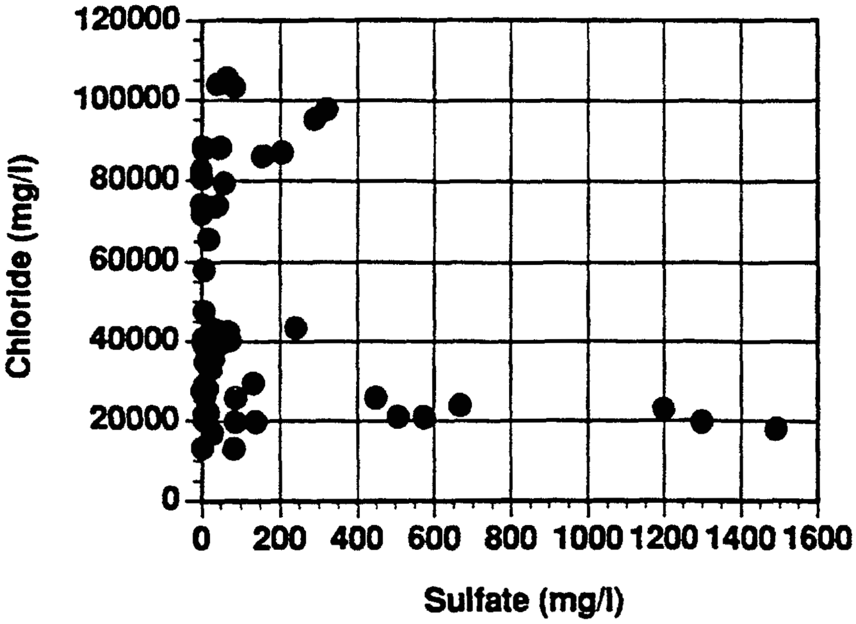

Figure 1. A plot of the sulfate vs. chloride concentrations showing the increase in sulfate at chloride concentrations near that of seawater (19,375 mg/l). This is probably due to water breakthrough from past seawater flooding in Field A.

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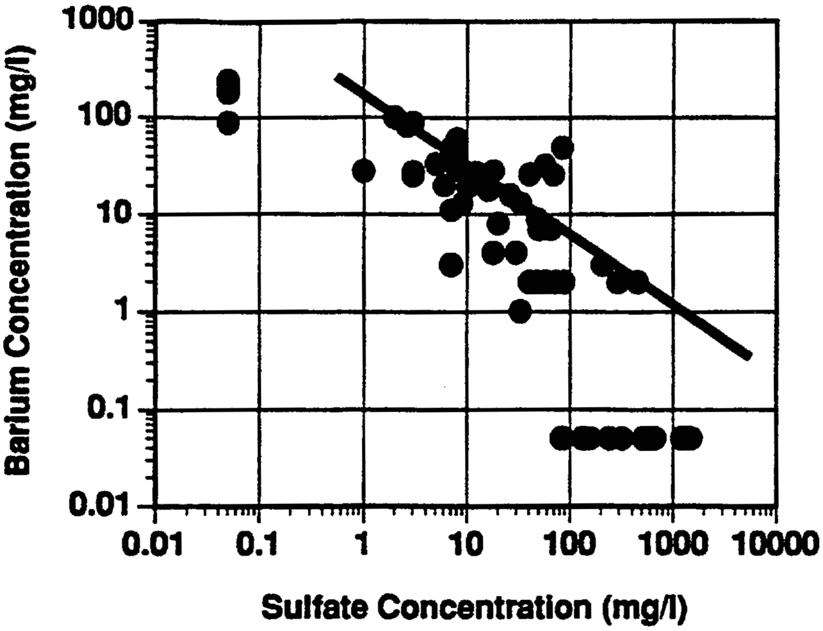

Figure 2. The concentrations of barium and sulfate in the produced waters from Field A illustrating when one variable is high, the other is low.

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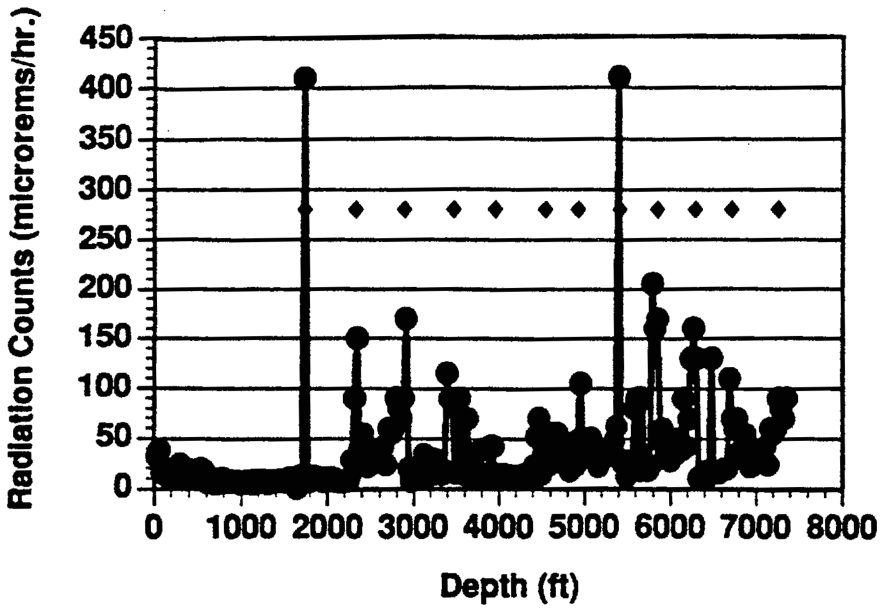

Figure 3. The radiation readings in well 5 from Field B vs. depth. The dark diamonds are the locations of the gas lift valves in the well.

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Control of NORM at Eugene Island 341-A

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ABSTRACT

A field study at Eugene Island 341-A, an offshore production platform in the Gulf of Mexico, was conducted to develop strategies for the cost-effective prevention of NORM (Naturally Occurring Radioactive Materials) deposits.

The specific objectives of this study were to:

- Determine the root cause for the NORM deposits at this facility, utilizing different diagnostic techniques.
- Consider all engineering options that are designed to prevent NORM from forming.
- Determine the most cost-effective engineering solution.

An overall objective was to generalize the diagnostics and control methods developed for Eugene Island 341-A to other oil and gas production facilities, especially to platforms located in the Gulf of Mexico.

This study determined that the NORM deposits found at Eugene Island 341-A stem from commingling incompatible produced waters at the surface. Wells completed in Sand Block A have a water containing a relatively high concentration of barium, while those formation brines in Sand Blocks B and C are high in sulfate. When these waters mix at the start of the fluid treatment facilities on the platform, barium sulfate forms. Radium that is present in the produced brines co-precipitates with the barium, thereby creating a radioactive barium sulfate scale deposit (NORM).

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The barium sulfate deposits (and hence NORM) can be prevented by maintaining improvements in the current chemical scale inhibition program. Keys to an effective prevention program are the continual, reliable injection of an appropriate scale inhibitor chemical at an effective dosage, and ahead of the point where scaling conditions begin.

INTRODUCTION

Study Objectives/Strategy

This study is a part of a larger research program to develop and test concepts for preventing NORM deposits. The premise behind this study is that it is usually **more cost-effective to have a proactive versus a reactive NORM strategy**. That is, it is better to implement measures to **prevent NORM deposits**, versus allowing these radioactive solids to form and then coping with the disposal costs.

NORM solids in oil field operations typically are caused by the incorporation of a small amount of radium present in the water into common scale deposits, especially barium sulfate. Thus, a strategy to avoid creating NORM deposits is to prevent the precipitation of the common, dominant scale. This has the benefit of preventing the dominant scale, which itself can be an operational problems, as well as avoid a NORM deposit.[1,2]

We used a wide variety of diagnostic methods to determine the causes for NORM deposits at Eugene Island 341-A. This provides us a wide body of evidence to identify the problems at this facility, plus this study provides an opportunity to determine the value of using these diagnostic methods in a real field situation. We also consider several options to prevent NORM at Eugene Island 341-A, and recommend an improved scale inhibition program as the best control measure.

Another outcome from this effort was to generalize the Eugene Island 341-A study approach into a NORM prevention guidebook. This manual takes the user through a systematic process to identify the causes and feasible engineering solutions to a NORM problem. It also helps the user to select the most cost-effective control option.

Historical NORM Problem

There has been a history of scale and NORM clean outs at the facility. The most recent clean out occurred in June of 1993. All of the vessels contained a mixture of formation sand and radioactive barium sulfate (NORM).

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It is difficult to accurately estimate the total cost of the NORM problem at Eugene Island 341-A. There is some incremental cost in the vessel clean out procedures to isolate and drum NORM contaminated sand and scale. Once contained, the estimated disposal cost for a single drum of NORM contaminated solids can be several hundred dollars. Between 30 and 50 drums of NORM contaminated solids resulted from the June 1993 clean-out. Additional (and hard to quantify) costs include administrative efforts to tag and track the NORM waste, storage costs, and future environmental liability.

BACKGROUND — RECENT AND CURRENT OPERATIONS

Field/Geologic Information

Eugene Island 341-A is located approximately 75 miles offshore in the Gulf of Mexico. Production began at this platform in 1982.

It is a complexly faulted, salt-cored anticlinal closure. The field is divided into numerous, separate sand bodies by small (100–200') faults. The field is primarily an oil producer with three main productive sands. The focus of this study is on the 6 oil wells completed in the 7400' Sand (A-1, A-2, A-3, A-8, A-10, and A-13) because these produce all of the water.

Based on limited data, the 7400' Sand is thought to be fairly mineralogically consistent throughout the field. It is typically an unlithified, fine to very fine grained, sub-angular to angular, moderately well sorted, immature, feldspathic quartz sand. Other than occasional calcareous cements, the sand shows almost no diagenetic alteration to its mineralogical make up.

Production comes from three different sand Blocks: A, B, and C in the 7400' Sand. As we describe later, a key to the NORM problem is understanding the differences in water chemistry for these formation waters. The water chemistry is nearly the same for Sand Block B and C wells, but differs considerably from those wells completed in Sand Block A.

Facilities Information

Figure 1 is a schematic showing the main path of the produced water in the topsides facilities. Five of the wells enter via the high pressure (HP) header (approximately 900 psi). Note that fluids produced from the Block B/C wells (A-2, A-3, and A-8) enter the HP header first, then commingle with production from Block A wells (A-1 and A-13). Well A-10 (from Block A) is produced into the low pressure (LP) header (approximately 150 psi).

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The two-phase separators only remove gas; oil and water are sent from the separators to the Chemelectric treater to produce sales quality oil. In recent operations the intermediate pressure (IP) bulk separator sometimes is bypassed; fluids then go directly from the HP to the LP bulk separator.

The bulk of the produced water exits the Chemelectric and is treated further (Sump Surge, then the Tridair) to reduce the oil concentration to a level acceptable for ocean discharge. The Tridair is a three-stage flotation cell device that promotes the gravity separation of dispersed oil drops and floats them to the top of the vessel. The oil-rich froth is skimmed off and recycled to the Chemelectric, and the cleaned water is discharged overboard. The Tridair is being replaced with a more modern oil removal unit in 1995. Process temperatures are in the range of 100°F to 150°F.

Production Information

Figure 2 presents the water production data for the oil wells at Eugene Island 341-A. We show the rates for various groupings of wells because of their common water chemistries and the manner in which these brines commingle. Water from Wells A-2, A-3, and A-8 from Blocks B/C mix in the HP header with production from Sand Block A Wells A-1 and A-13. Fluids from the remaining oil well, A-10 (currently shut in), enters via the LP header and mixes with the fluids from the other wells in the LP bulk separator.

Water production from Sand Block A wells (55 to 75% of the total) has been greater than that from Blocks B/C, both in the HP header and at the LP separator. As discussed later (**Calculated Scaling Tendencies**), this mixing ratio is important in determining the probability of barium sulfate/NORM deposition at a given location in the facilities.

Recent/Current Chemical Treatment Program

Scale Inhibitor Products

Three different scale inhibitors have been used during the course of this study:

1. Inhibitor A, a phosphonate — prior to June 1993 to mid-1993.
2. Inhibitor B, a polymer — mid-1993–January 1994
3. Inhibitor C, a phosphate ester — January 1994– present

Inhibitor A was selected initially because of its very good water compatibility, especially its tolerance to high calcium produced waters. Unfortu-

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nately, this excellent calcium tolerance also makes Inhibitor A a relatively poor scale inhibitor, and increases its cost per gallon.

Based upon scale coupon data (detailed in a later section) and good experiences with Inhibitor B elsewhere, we switched to B in mid-1993. This inhibitor performed quite well through November of 1993. Thereafter, the build-up on the scale coupon indicated it was no longer effective. Tests by the service company in January 1994 indicate the Inhibitor B was no longer compatible with the produced water chemistry. This might be related to well workovers begun in December 1993. This disruption in normal operations created fluctuations in individual well rates and thus fluctuations in the water chemistry of the mixed streams.

Inhibitor C was tried next in this field evaluation. Field performance indicated it is compatible with the current produced water chemistry and at first had mediocre success in preventing barium sulfate. Further adjustments to improve the reliability of chemical injection of product C have made this application a success.

Laboratory measurements of scale inhibitor performance in synthetic Eugene Island 341-A brine show the relative effectiveness to be Inhibitor C = Inhibitor B > Inhibitor A.

Scale Inhibitor Application

Just as, or even more important, than the selection of scale inhibitor product and its proper dosage, is the successful application of the inhibitor into the water. So far, scale inhibitor has been delivered via a chemical pump at the topsides facility; there have been no down hole treatments.

A <u>key point</u> is that scale will form if the chemical injection pump is out of service (zero dosage), no matter how good the inhibitor is. **<u>Scale will form during periods of no chemical injection</u>**; once the chemical pump stops, the inhibitor concentration in the system rapidly goes to zero. This is an important consideration at Eugene Island 341-A because there have been episodes of intermittent performance by the chemical pumps (pump failures, clogged valves, etc.) Closer monitoring to verify there is uniform chemical injection has improved this inhibition program.

At one time, inhibitor injection was into the wellhead at A-13. This has the decided **<u>advantage of placing the chemical into the water before scaling conditions begins</u>** at this facility. Scale inhibitors are less effective if added after substantial precipitation starts. A disadvantage of this location was that inhibitor injection was disrupted because that particular well went down occasionally. The

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injection is now at three points (A-1, A-3, and A-8 wellheads) for increased reliability.

DIAGNOSTICS TO DETERMINE THE CAUSES OF NORM

As detailed below, the several pieces of evidence we collected all point to <u>commingling of incompatible produced waters topsides as the root cause of NORM at Eugene Island 341-A.</u>

Water Chemistry

Table 1 summarizes water analyses from several points in the facility. Observations from these data are:

- The Block A water is high in barium and total salinity.
- The Block B/C water is high in sulfate and very high in total salinity.
- The water chemistry in the separators, Sump Surge, and Tridair all are consistent with the expected mixture of Block A and B/C waters (55–75% Block A type brine).
- Radium measurements suggest NORM forms after brines commingle, not down hole.

The large variations in sulfate, barium, and total dissolved solids (TDS) indicate differential transport and flow into small fault blocks with the 7400' Sand. It is postulated that water and hydrocarbons are being brought up major faults from a greater depth, recharging the reservoirs and causing anomalies in physical properties around the fault. For example, water analyses show the TDS (total dissolved solids) and sulfate concentrations are higher near the fault; i.e. for B Sand Wells A-3 and A-8. Conversely, A Sand wells (A-1, A-10, and A-13) have high barium and lower TDS.

Table 2 shows the measured dissolved radium concentrations in samples collected in January 1994. The radium levels are about the same in both Block A and Block B waters (total of 500–600 picoCuries/liter). This is a relatively high radioactivity, but not untypical for Gulf of Mexico produced waters. If radium is indeed inherent to the 7400' Sand, we can not focus on a single "high radium" well for special treatment. That is, we expect about the same, relatively high dissolved radium concentration in the produced water from any well (from any block) completed in this sand.

One other observation is that the total radium levels are lower in the separators, etc., than the well head samples. This suggests active loss (NORM deposition) when we sampled for radium in January 1994 during a down period

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for the inhibitor pumps. As a follow-up, we filtered and re-analyzed some of these same samples later. The well head samples (A-1, A-3, and A-8) had about the same radium concentrations; this suggests that <u>all of the radium at the well heads are in a soluble form</u>. In contrast, the filtered Sump Surge sample shows even lower radium concentrations, indicating <u>significant radium is associated with the solids in this vessel</u>.

Calculated Scaling Tendencies

Figure 3 shows the calculated barium sulfate scaling tendencies for hypothetical mixtures of brines produced from Block A and B/C. These calculations indicate:

- There is no scaling tendency for individual well brines.
- The scaling tendency is significant for any mixture of Block A and Block B/C brines, including the expected mixing ratio of 55–75% Block A water.
- The theoretical maximum (uninhibited) deposition rate is 15–20 mg/l; for a platform total production of 4000 BWPD this translates to 21–28 lb barium sulfate scale/day.

<u>Conclusions from scaling tendency calculations are:</u>

- Scale deposition will begin once Block A and Block B/C waters mix (starting in the HP header) if there is no effective scale inhibitor present.
- Positive barium sulfate scaling conditions will continue through the remainder of the water treatment system (from the separators to water discharge).
- The barium sulfate scale tendency is positive for sump pile water (has 1800 mg/l sulfate) added occasionally to the Sump Surge Tank (has moderate barium concentration). The volume of high sulfate water has decreased significantly with the installation of an enclosed tank to replace the sump pile.

The topsides scaling tendency for barium sulfate here is moderate (typically Saturation Index (SI) is $0 < 1$); a regime where the scale is likely to adhere to surfaces (sand grains, pipe walls, etc.). By definition, $SI < 0$ means the water is undersaturated and will not form scale. $0 < SI < 1$ is a moderate scaling tendency, and $SI > 1$ is a high scaling tendency.[3]

Other calculations indicate that there is little or no positive scaling tendency with respect to calcium carbonate. In contrast, the calculated tendency to form iron oxides is extremely high if there is any available oxygen.

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Radioactivity (Scintillation) Surveys

Figure 4 shows the results of scintillation meter readings taken throughout the topsides facility in January 1994. Significant observations:

- In all cases the radioactivity readings are very low at the well heads.
- High readings (first NORM deposits) begin in the HP header after Block A produced water enters and mixes with the Block B/C produced fluids.
- The separators show high readings in the vessel bottom, suggesting a settled accumulation of NORM contaminated solids.
- There are consistently high readings all around the Tridair water clarifier.

Collected Solids/Analyses

Separator Solids

Solids collected from the vessels during the clean out operation in June 1993 were analyzed via X-ray diffraction (XRD) and scanning electron microscope (SEM). Important findings are:

- The solids in the vessels were mostly sand/sludge with some barium sulfate (NORM).
- The barium sulfate scale is associated more with the larger sized particles.
- The scale largely is present as a growth on formation particles. That is, the produced sand acts as a nucleating site for the radioactive barium sulfate scale.

Figure 5 shows SEM photographs illustrating the growth pattern of NORM scale on individual sand grains.

Pipe Scale/Tridair Solids

Eugene Island 341-A has a history of scale build-up in the overboard line. Previous analyses indicate it is predominantly iron oxide. The most likely explanation for its formation is that oxygen (air intrusion at the Tridair, at hatch covers and plastic pipe joints, or elsewhere) combines with the dissolved iron and precipitates as iron oxide. This scale problem can be reduced by locating and fixing these air intrusion locations.

A pipe scale sample removed in January 1994 was unusual because it was not predominantly iron compounds, but rather half of it was radioactive barium sulfate. This was during a period of ineffective scale inhibition (when Inhibitor B was not compatible with produced water and when chemical injection was off).

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Scale Coupons

Table 3 summarizes data from a scale coupon located on a recirculation line at the Tridair. These data show:

- Moderate scale build-up in early 1993 — when injected Inhibitor A. Measured deposition was several hundred mg/sq. in./yr. The target rate is under 100 mg/sq. in./yr.
- Reduced or no scale build-up from July–November 1993 — when injected Inhibitor B.
- Scale accumulation in December 1993–January 1994 — when Inhibitor B no longer was compatible with the produced water chemistry.
- A short period in January of extremely high deposition rate when no chemical injection was possible. The 15,644 mg/sq. in./yr rate illustrates how high uncontrolled scaling can be here.
- Much reduced, but moderate, scale build-up in late January–February 1994 — after starting Inhibitor C.
- Reduced or no scale accumulation after improved reliability of chemical injection.

Treatment continues with Inhibitor C. Closer monitoring of its effectiveness has been instituted, such as more frequent inspection of scale coupons.

X-Ray of Piping

X-rays of platform facilities are performed routinely to determine changes in pipe wall thickness (corrosion). We wanted to determine if this method would have any value as a measure of scale accumulation in a facility.

There was a routine, scheduled X-ray survey done at Eugene Island 341-A in February 1994 for purposes of monitoring corrosion. Several extra X-rays also were taken at suspected points of NORM pipeline accumulation. These X-rays showed accumulations of 0.15 to 0.5 inches of scale in the HP header, water dump line of the HP separator, and a line at the Tridair water clarifier. This appears to be a useful, nonintrusive monitoring method to identify scale deposits. Another advantage of this approach is that these data can be collected at little incremental cost if done in conjunction with planned, routine surveys for corrosion monitoring.

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POSSIBLE NORM CONTROL OPTIONS

Scale Inhibition Program

This is the recommended choice. It should be possible to prevent NORM accumulation for a scale inhibitor cost of $10,000 to $20,000/year at Eugene Island 341-A (assumes water production remains at approximately 4,000 bbl/day). To be completely successful, the scale inhibition program must maintain recent improvements:

- reliability for scale inhibitor injection of nearly 100%.
- chemical injection point ahead of where NORM starts in the HP header.
- increased monitoring (frequent coupon checks, rechecks of inhibitor compatibility and effectiveness, frequent radioactivity surveys, etc.).

Avoid Mixing Incompatible Waters

Process Waters Separately

Conceptually, if you could process production from Sand Block A and B/C separately, these incompatible waters would never mix and hence no NORM would form. It is unlikely this is a practical option for Eugene Island 341-A. This approach may be easier to implement in the design of new facilities if this problem is anticipated.

Shut in Some Wells or Recomplete in Different Zone

If production from either the 7400' Sand Block A or B/C were stopped, mixing incompatible brines at the surface would be eliminated. This is not a practical option unless oil production fell to an uneconomic point for all of the wells in one sand block.

One could shut in such wells completely, or recomplete the wells at a different horizon where the formation water is compatible with the remaining producing wells.

Sand Control

Reducing the amount of sand produced will reduce the cost of the NORM problem. This will decrease the volume of contaminated solids, if the scale inhibitor fails to prevent NORM deposition on the produced sand.

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Remove NORM Chemically

This is not a practical option for remediating topsides contamination such as exists at Eugene Island 341-A. There are commercial products available that have a limited capability to dissolve barium sulfate (and hence NORM). These dissolvers are slow acting and expensive. They are not intended to be applied as an agent to remove large amounts of barium sulfate such as required to decontaminate whole vessels. They have been cost-effective in some down hole stimulations where removing only a small amount of scale in the perforations and near wellbore area significantly increased production.[4]

Take No Action

Scaling rates and the accumulation of NORM would be very high in the absence of any control program. The annualized cost to remove and dispose of NORM, plus the other negative impacts of scale deposition make this a poor alternative.

NORM CONTROL GUIDEBOOK— GENERALIZING THE PROCESS

We generalized the process used in the Eugene Island 341-A NORM study and created a manual called the *NORM Control Guidebook* for our operating companies. Figure 6 shows the overall process flow diagram from this manual. It includes worksheets and examples to lead the user through the steps of diagnostics, selection of control measures, and a rough economic evaluation for a specific site.

CONCLUSIONS

1. NORM at Eugene Island 341-A stems from mixing incompatible produced waters at the surface (some high in barium, some high in sulfate). The resulting barium sulfate scale is made radioactive (becomes NORM) by co-precipitating radium from the produced water into the deposit.
2. Radioactive barium sulfate (NORM) can be largely prevented at Eugene Island 341-A by injecting a scale inhibitor in the surface facilities. A totally effective scale inhibition program requires maintaining improvements in the reliability of injecting the chemical inhibitor.
3. The different diagnostics used in this study (e.g., water chemistry, production data, study of the facility layout, scale coupons, radioactivity surveys, and X-Ray) all provided useful information at a low cost and required little time.

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These same techniques may be applied to diagnose and monitor NORM problems at any production facility.

4. A possible aggravating source of NORM has been oil and water occasionally pumped from the sump pile to the Sump Surge Tank. This sump pile water has a high sulfate concentration and is incompatible with the water in the Sump Surge Tank (significant barium content). The recent replacement of the sump pile with an enclosed tank will decrease the volume of that incompatible water source.

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Table 1

Typical Water Analyses For Eugene Island 341-A

Sample Location	Na	Ca	Mg	Sr	Ba	Fe	All Concentrations in mg/l Cl	SO4	HCO3	pH	Calculated ** SI(BaSO4)	Calculated ** Scaling Capacity lb scale/1000 bbl water
Block A wells	60000	4000	1000	150	50	25	95000	10	50	6.50	-0.24	0
Block B wells	110000	4000	1200	150	1	50	190000	500	50	6.00	0	0
HP Bulk Sep.	70000	3700	1200	150	8	30	120000	200	50	6.00	0.35	3
IP Buk Sep.	70000	3700	1250	150	6	30	125000	240	n/d	n/d	0.32	2
LP Bulk Sep.	80000	3700	1200	150	9	25	130000	230	50	6.00	0.5	4
Chemelectric	83000	3600	1300	150	12	30	132000	210	n/d	7.00	0.6	5
Sump Surge	80000	3600	1250	150	8	35	130000	250	25	5.9	0.49	3
Sump Pile	10200	640	840	n/d	2	7	18000	1800	150	6.2	0.03	0

NOTE: n/d = not determined
**Calculated at T =125 F, P = 14.7 psia

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Table 2

Radium Concentration — Produced Waters From Eugene Island 341-A

Sample Location	Radium 226 picoCuries/liter	Radium 228 picoCuries/liter	Total Radium picoCuries/liter	Comments
January 11, 1994 samples — analyzed as is				
Well A-1	192.2	401.6	594	water from Sand Block A
Well A-3	98.71	347.3	446	water from Sand Block B
Well A-8	99.36	454.5	554	water from Sand Block B
HP Bulk Separator	234.2	479.2	713	
Int. Bulk Separator	67.56	104.1	172	
LP Bulk Separator	35.6	86.69	122	
Chemelectric	71.13	84.19	155	
Sump Surge	97.4	140.3	238	
Tridair	105.5	131.5	237	
Samples analyzed in March, 1994 — samples filtered				
Well A-1	127.3	396.6	524	Filtered wellhead samples have same radium as above — this says radium is dissolved
Well A-3	112.6	387.8	500	
Well A-8	85.53	416.7	502	
Sump Surge	9.5	50.6	60	Low radium in filtered sample —this says significant radium is in solids in Sump Surge sample

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Table 3

Scale Coupon Results -- Eugene Island 341-A

Coupon #	Date In	Date Out	Days Exposed	Deposition mg/sq. in./yr	Comments
A-836	4/16/93	5/30/93	45	400	
A-8446	5/30/93	6/9/93	11	800	
A-833	6/9/93	6/22/93	14	150	Changed from scale Inhibitor A to Inhibitor B
A-834	6/22/93	7/29/93	38	80	
C-116	7/29/93	8/30/93	33	0.4	
	8/30/93	Nov-93		Low	Visual observations that coupon was clean during this period
C-115	Sep-94	1/6//94	116	7200	Platform upsets due to well workovers. Evidence that Inhibitor B no longer compatible with produced water. Visual evidence that high deposition did not start until Dec-93.
C-124	1/6/94	1/23/94	18	15700	No inhibitor could be pumped during this short period. This coupon indicates maximum, uncontrolled scaling rate
C-162	1/23/94	2/22/94	31	700	Switched to scale Inhibitor C. Not certain if mediocre performance is fault of inhibitor;problems maintaining continuous chemical injection.
	Mar-94	May-94		6.2	Improved reliability of scale inhibitor injection
B-885	2/24/95	3/24/95	29	275	CaCO3 scale at Chemelectric
B-670	3/24/95	4/24/95	32	155	CaCO3 scale at Chemelectric

Note : Scale coupon located at Tridair or Chemelectric

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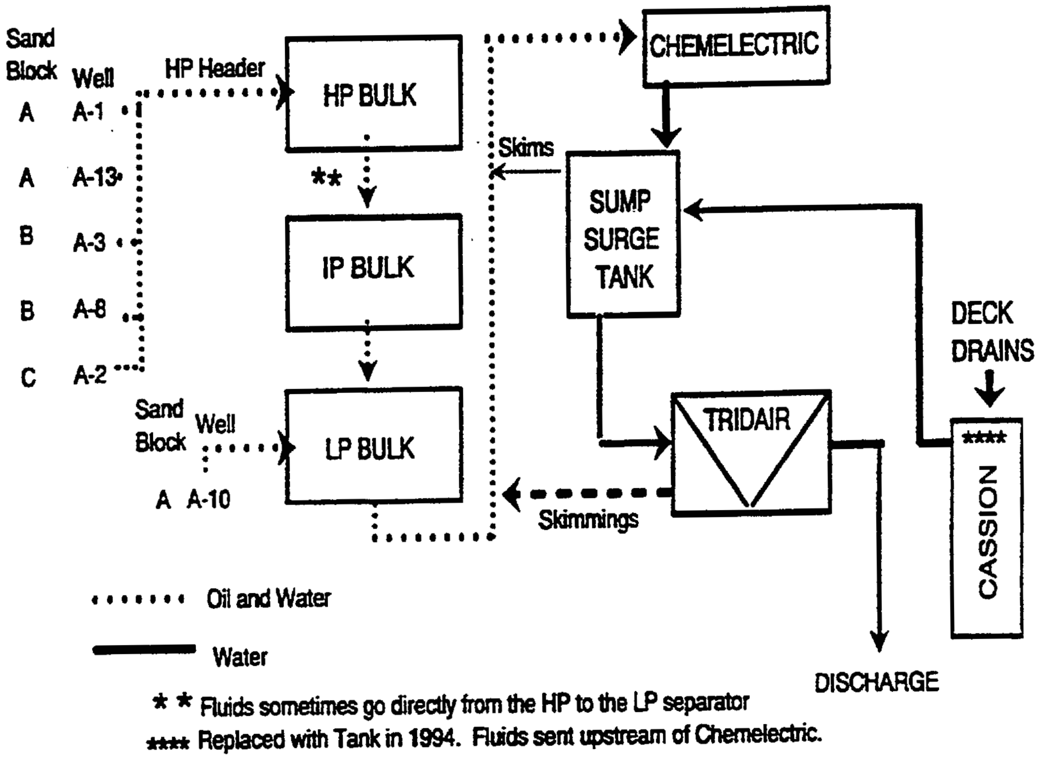

Figure 1. Eugene Island Surface Facility - Main Flow of Water

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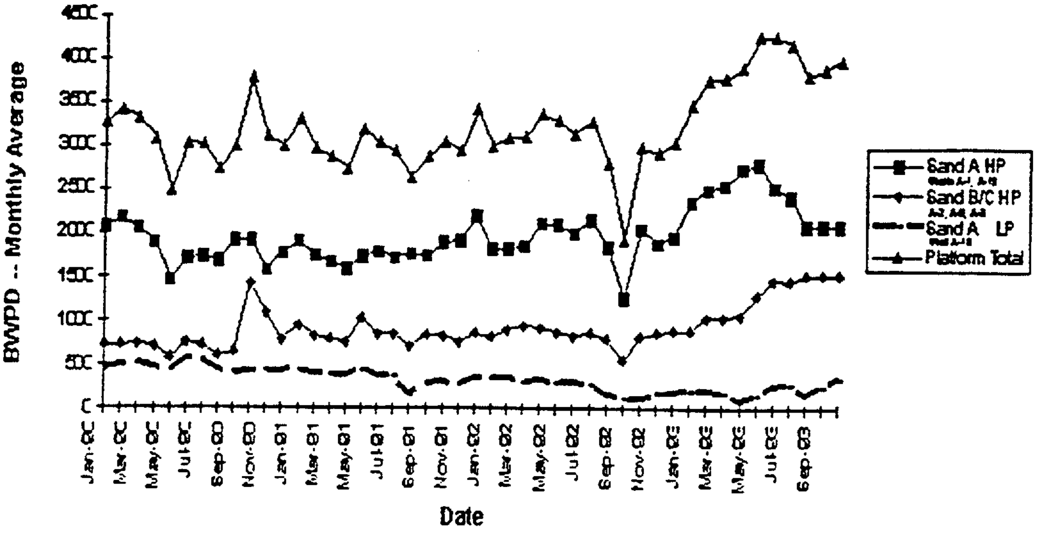

Figure 2. Water Production from Eugene Island 341-A

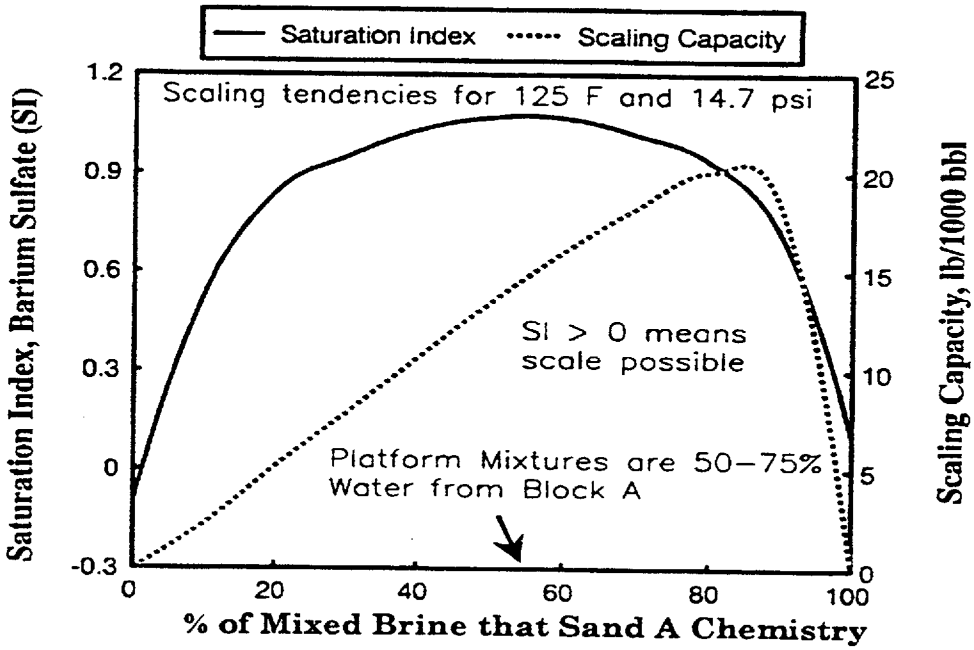

Figure 3. Calculated Scaling Tendency and Capacity for Barium Sulfate for Mixtures of Block A and Block B Waters

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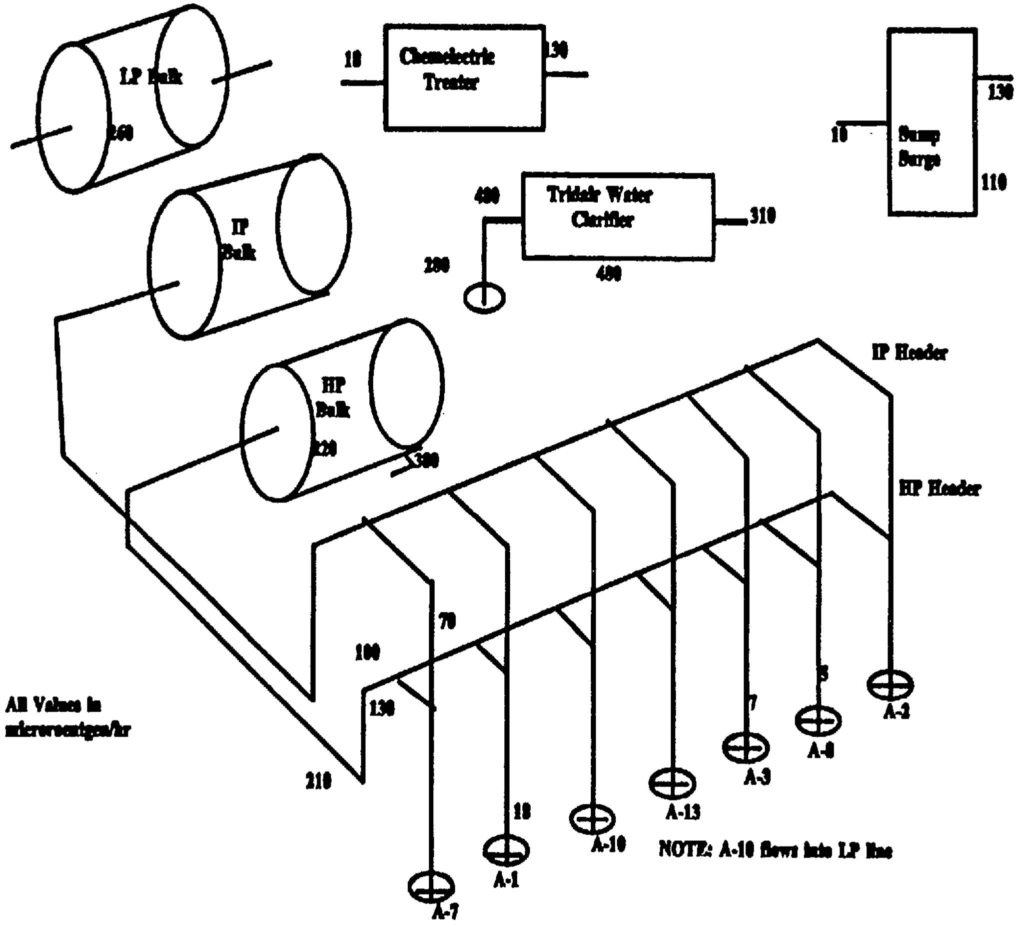

Figure 4. Eugene Island 341-A Radioactivity Survey, January 1994

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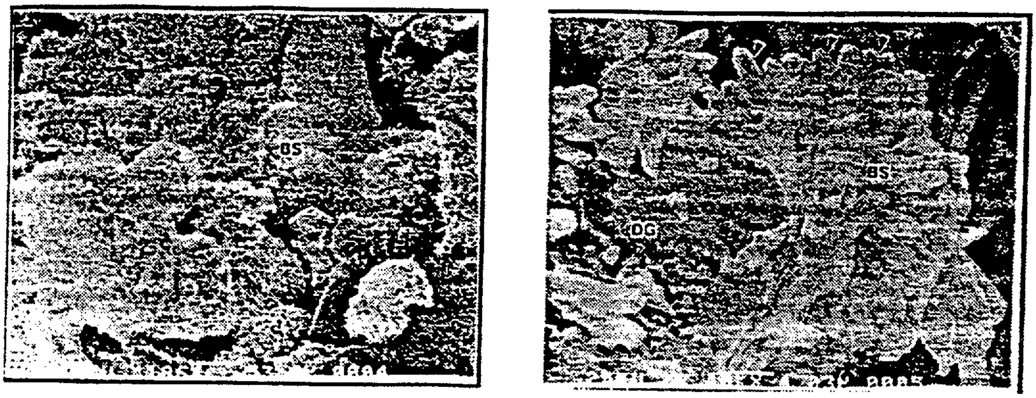

a. Textural views showing barium sulfate (BS) crystals nucleating on produced sand.

b. Higher magnification showing fan-shaped cluster of barium sulfate (BS) nucleating on a detrital grain (DG). Note the individual euhedral rhombic crystals (arrows).

Figure 5. SEM Photos of Solids from Intermediate Pressure Bulk Separator

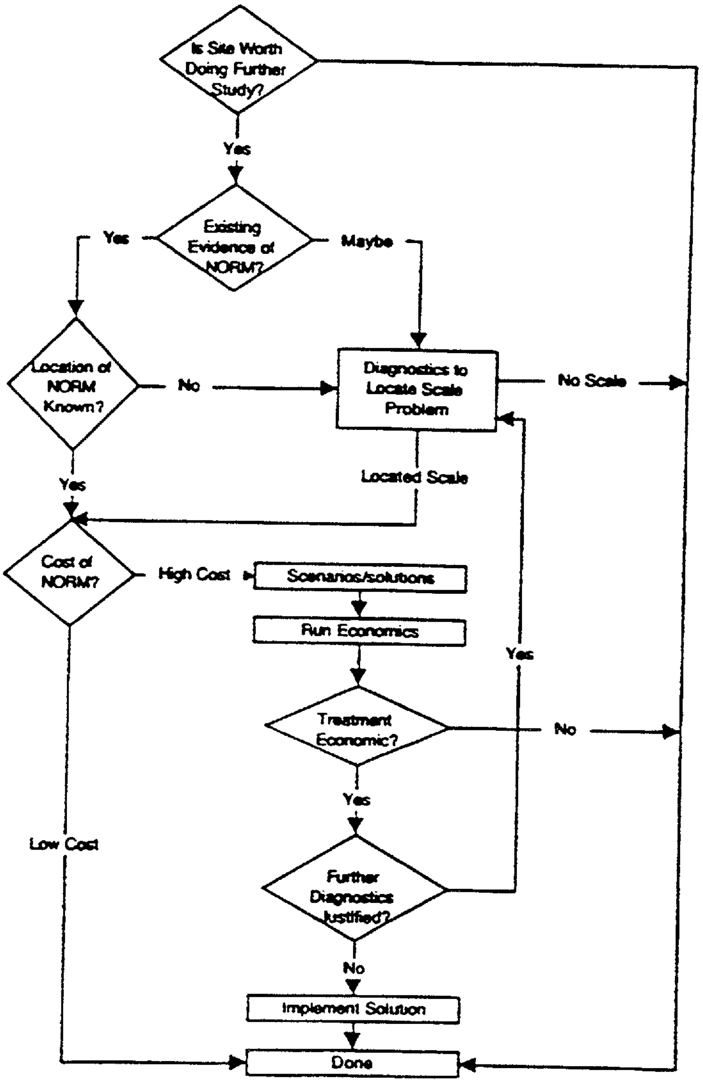

Figure 6. NORM Control Flowchart

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A COMPARISON OF NORM SCALE DISSOLVERS

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Key Words: NORM, scale, dissolving agents

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ABSTRACT

In laboratory tests, a variety of commercially-available solvents have been compared for selective dissolution of NORM (naturally-occurring radioactive material) from geothermal scale deposits. These scales consist primarily of silicates contaminated with radium-226 and radium-228 that co-precipitate with barium sulfate. The dissolvers compared in this study generally consist of high-pH chelating agents. Although the dissolvers perform optimally above boiling temperature, economic field application is best achieved at lower temperature conditions. A solvent that consistently performed well in the laboratory studies is composed of the chelate, diethylenetriaminepentaacetate, DTPA, and an oxalate scale converter. This product was successfully field tested in a geothermal brine injection well. The removal of NORM contaminated geothermal scale from piping and wells is extremely costly compared to the cost of deposition control by commercially-available scale inhibitors.

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INTRODUCTION

Many processes that obtain resources from the earth, for example, oil, geothermal and mining production, result in the co-production of aqueous liquids. These liquids may become supersaturated in rapidly precipitating minerals. Alkaline earth salts, such as calcium, strontium and barium sulfate, are frequently found in significant concentrations in produced fluids. During fluid handling, especially where fluid temperatures are reduced, these salts precipitate as scales. The scales may be radioactive, containing low levels of naturally-occurring radium, thorium and lead.

Geothermal fluids contain thermal energy in vast amounts that can be utilized to produce electrical power. In one process for producing electrical power, naturally pressurized, hot geothermal brine is recovered from deep wells and suddenly depressurized or flashed. Flashing cools the brine while reducing its pressure, converting some of the brine to steam used to power steam turbine generators. Cooled geothermal brine is typically reinjected to replenish the aquifer and maintain reservoir pressure.

Geothermal brines are often saturated or nearly saturated in many salts and minerals. This is especially true at the Salton Sea geothermal field located in extreme southeastern California. As geothermal brines are flashed, the salts and minerals may become supersaturated by concentrative and temperature effects. Some minerals, particularly silicates, form small, poorly-crystalline particles that precipitate very slowly. Other minerals, particularly sulfates and sulfides, precipitate relatively rapidly as crystalline minerals in brine-handling equipment. Barium sulfate (barite) presents an annoying problem in many geothermal systems since it begins to precipitate from cooling brine at temperatures as high as 160°C.

Some geothermal scale deposits exhibit radioactivity associated with lead sulfide (galena), calcium fluoride (fluorite) and barite (Gallup and Featherstone, 1995a). Radioisotopes detected in geothermal scale deposits include radium-226, radium-228, actinium-227, lead-214, bismuth-214 and thorium-232. Processes to inhibit NORM deposition from geothermal operations have recently been developed (Gallup and Featherstone, 1993a, 1994, 1995b). However, when inhibition methods are ineffective, NORM-laden scales may require chemical (D'Muhala, 1987; Paul and Fieler, 1992; Fielder, 1994) or mechanical removal. The objective of the present study was to evaluate scale dissolution agents to remove existing NORM scale from brine-handling equipment and reinjection wells.

NORM DEPOSITION & INHIBITION

Geothermal fluids produced from wells at the Salton Sea geothermal field are processed through a series of vessels to gather steam and inhibit silica scaling (see Figure 1). In a typical Salton Sea resource production facility, brines are sequentially flashed in the wellhead separator (WHS), standard pressure crystallizer (SPC), low pressure crystallizer (LPC) and atmospheric flash tank (AFT). Brine is then processed in a series of clarifiers to inhibit iron silicate scaling by forming a non-adhering sludge before traversing kilometer-long injection pipelines to offset injection wells. These hyper-saline brines exhibit total dissolved solids concentrations (TDS) ranging from 15 to 30 wt. %, and are further concentrated in the series of flashing steps. These brines, produced from the reservoir at temperatures ranging from 230 to 330°C, consist primarily of dissolved sodium, potassium and calcium chloride salts. The brines produced from the Salton Sea geothermal reservoir also contain many heavy metals, barium, sulfate, and fluoride. The primary dissolved gases in the brines include carbon dioxide,

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ammonia and hydrogen sulfide. Table 1 presents a representative analysis of Salton Sea geothermal brine.

Iron silicate scales begin to precipitate from Salton Sea brine below about 200°C at the WHS and farther downstream (Gallup and Reiff, 1991). Near wellheads and wellhead separators, minor amounts of radioactive galena, PbS, may deposit as mixtures with iron silicate. Barium sulfate is predicted to reach saturation in Salton Sea hyper-saline brine at about 160°C using a proprietary UNOCAL scale prediction model. Barite, $BaSO_4$, and fluorite, CaF_2, exhibit prograde solubility, so as Salton Sea brine decreases in temperature upon flashing through the crystallizers and AFT to an injection temperature of about 105°C, barite and fluorite appear in sludges and scales downstream of the LPC (see Figure 1). Downstream of the LPC, a copper arsenide scale, Cu_3As, also co-deposits with $BaSO_4$ and CaF_2.

As discussed above, traces of radium-226, radium-228, potassium-40, throrium-232 and other decay series nuclides are present in Salton Sea brines. The radium nuclides in brine are present in concentrations approaching about 4 Bq/L, where 1 becquerel (Bq) is equivalent to 27 picocuries (pCi). Upon operation of geothermal power plants at the Salton Sea field, it was discovered that scale deposits produced in the brine manipulation process contained low levels of radioactive material. Scintillation counter and gamma spectroscopic specific nuclide activity analyses detected various nuclides and emission of small amounts of alpha, beta and gamma radiation. Precautions were taken during handling of the scale to insure the safety of personnel exposed. Radium, exhibiting chemistry similar to barium, co-deposits with barite to yield NORM-laden scale and sludge:

$$M^{2+} + SO_4^{2-} \rightarrow MSO_4 \quad (M = Ba, Ra) \qquad (1)$$

In Reaction 1, the limiting reagent in Salton Sea brine is sulfate. Concentrations of the radium nuclides, Ra-226 and Ra-228, in scale are similar and range from about 3 - 9 Bq/g, each. Scales deposited from Salton Sea geothermal brines often exceed the NORM limit of ~0.2 Bq/g established by the states of Louisiana and Mississippi (Gray, 1990). The presence of NORM in Salton Sea geothermal deposits is analogous to situations encountered in the petroleum industry, where barite scales containing low concentrations of radium are deposited from oil-field brines (Smith, 1987; Waldrum, 1988; Gray, 1993).

An investigation designed to solve the problem of NORM deposition and disposal at the Salton Sea field was consequently undertaken. Using a systematic and scientific approach, the sources of radioactivity in the sludge and scale deposits (primarily radium) were determined by nuclide analysis. The chemistry and processes responsible for NORM deposition were elucidated by studying barite deposition from the brine. Brine and scale analyses confirmed that radium-substituted barite was deposited from brine downstream of the HPC at temperatures < 160°C. Radium concentrations generally correlated with barite concentrations in scale deposits (Rogers and Lund, 1992). In Salton Sea geothermal scales, radium appears to deposit as radium sulfate with barite (see Reaction 1), thorium as a fluoride with fluorite, and lead as the sulfide.

Processes to inhibit NORM and unwanted $BaSO_4$ and CaF_2 deposits from Salton Sea geothermal brines were investigated. These studies led to the development of patented processes to inhibit silicate, barite, fluorite and NORM deposition from Salton Sea brines, *vide supra* (Gallup and Featherstone, 1993b). The deposition inhibition processes were designed to return dissolved radium in brine to the geothermal reservoir via normal brine injection disposal methods. Although NORM, barite and fluorite scale deposition are successfully inhibited at Salton Sea resource production facilities by step-wise injection of 2 - 4 mg/kg of an

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alkylaminophosphonate threshold inhibitor into brine, traces of NORM scales are deposited downstream of the LPC. Furthermore, NORM, barite and fluorite scales deposit in the injection formation, thereby slowly reducing brine disposal capacity. Methods to predict and inhibit NORM deposition from oil-field brines have recently been described and are consistent with our studies of geothermal systems (Oddo and Tomson, 1994). The present study was undertaken to determine the efficacy of scale dissolvers to remove NORM scale deposits in piping that are not completely inhibited in the patented scale control process and to stimulate injection wells by removing skin damage.

NORM DISSOLUTION - LABORATORY STUDIES

Experimental. Three different types of NORM scales were examined in the laboratory studies - (1) iron silicate containing ~30 wt. % $BaSO_4$ and 9.3 Bq/g of radium-226; (2) barite/fluorite containing 7.4 Bq/g of radium-226; and (3) copper arsenide containing ~15 wt. % $BaSO_4$ and 3.7 Bq/g of radium-226 (see Table 2). Twenty grams of respective scale, as 8 - 10 mesh chips, were placed into a Teflon®-lined, stainless steel reaction vessel together with 100 mL of the respective scale solvent. Commercially-available dissolvers were applied in "as received" condition. The mixtures were heated to desired temperatures for 48 hours with stirring. Upon completion of the reactions, the reaction vessel was rapidly cooled and the resultant mixtures were discharged and filtered. Filtrates were analyzed for metals, and unreacted scales were washed with distilled water to remove entrained solvent, dried overnight at 100°C and re-weighed. Scales were analyzed by gamma spectroscopy for specific activities of the radionuclides at Controls for Environmental Pollution, Santa Fe, NM.

Dissolution in Waters. Scale retrieved from a Salton Sea resource production facility was examined for leachability of NORM by water. In laboratory tests, scale chips containing up to 16 Bq/g of radium-226 were leached for 30 days with distilled water (simulated rain water) and Salton Sea water (simulated worst-case groundwater) at ambient temperature. NORM, barite and fluorite were found to be completely insoluble in these leaching experiments. Groundwaters sampled around the Salton Sea geothermal facilities, where scale has been mechanically removed from piping by hydroblasting, show no nuclide concentrations (< 0.04 Bq/L) above natural background. These site assessment studies are consistent with the laboratory results that demonstrate NORM in the geothermal scale is insoluble in rain water and groundwater.

Scale Solvents. Attempts to leach NORM, barite and fluorite from scales with a variety of chemical solvents were partially successful. Tables 3 - 5 and Figure 2 show the results of scale dissolution tests performed in the laboratory. Water, acid and base were generally ineffective in dissolving NORM, as Ra-226, from the scales. Dissolver B, a solution of 25 wt. % tetrasodium-ethylenediaminetetraacetic acid, Na_4EDTA, was quite effective in dissolving scale and reducing resultant Ra-226 concentrations. Commercially-available barium sulfate scale dissolvers, Dissolvers E - K, used primarily in the petroleum industry (chelants, surfactants, sequestrants and converters in basic solution) dissolved and leached widely varying amounts of NORM from scale under rather rigorous reaction conditions. These tests indicate that dissolution of the three different scale types was best achieved above boiling temperature for up to 48 hours with stirring. Unfortunately, chemical cleaning of NORM scale in kilometer-long piping above boiling temperature with circulation and for extended periods in the field, is not particularly practical. Mechanical cleaning followed by disposal in a NORM disposal facility or

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a deep well is more cost effective than high temperature dissolution. In commercial practice, solvents would probably need to be applied below boiling temperature and spent materials would preferably be disposed in the geothermal reservoir (Gardiner, 1994).

Of the commercially-available dissolvers examined in this study, Dissolvers E, F, G and K, generally dissolved more scale and decreased Ra-226 concentrations better than Dissolvers H - J. Due to the proprietary nature of the commercial dissolvers, it is difficult to ascertain dissolution effectiveness as a function of composition. It appears that products containing blends of chelates, such as EDTA and DTPA, and possibly scale converters and surfactants, performed best in these tests. Strong sodium-EDTA solution prepared in the laboratory, Dissolver B, yielded results similar to several of the more effective commercially-available products. The scale dissolvers and nitric acid, Dissolver D, leached significant iron and copper from Scale #3, while caustic solution, Dissolver C, tended to leach silica from each of the scales. Chelating agents also reduced thorium concentrations by up to about 25% in the scales (data not shown).

Solvent F, consisting of both a chelate and scale converter, generally performed better than the other solvents. Chelating agents, such as EDTA and DTPA, are known to form strong complexes with both alkaline earth and heavy metals that result in mineral solubilization (Laitinen and Harris, 1975). For example, EDTA complexes with barium in barite:

$$BaSO_4 + EDTA \rightarrow BaEDTA^{2+} + SO_4^{2-} \quad (2)$$

Scale converters, such as carbonates and oxalates, are utilized in metathesis reactions to alter sulfate minerals. Sulfates are often converted to their corresponding carbonate or carboxylate forms that are more readily coordinated by the chelates:

$$BaSO_4 + Na_2CO_3 \rightarrow BaCO_3 + Na_2SO_4 \quad (3)$$

FIELD TESTING OF SCALE SOLVENT F TO CLEAN AND STIMULATE AN INJECTION WELL

Solvent F was selected for demonstration testing at a resource production facility due to its relatively successful effectiveness in dissolving barite/fluorite/NORM scale in the laboratory dissolution tests, and due to it's relatively low cost. Over the course of two years of operation, an injection well at the Salton Sea field suffered skin and formation damage as a result of iron silicate, copper arsenide and barite/NORM scaling. Formation damage by barite/NORM was confirmed by electron microprobe analysis of sidewall cores. It was estimated that the cost to mechanically clean the well and perform a re-drill would exceed $250,000.

The chemical supplier and a service company designed the coiled tubing, well stimulation treatment with Solvent F so as not to exceed a cost of $250,000. The injection well was first logged with a sinker bar, pressure/temperature/spinner and caliper. After an injection capacity test, the well was removed from service and flushed with 2400 m^3 (22 wellbore volumes) of pH modified steam condensate to minimize solvent contact with hyper-saline brine. (The solvent was shown to be incompatible with the brine in field jar tests.) The "as-received" solvent was diluted by 50% with steam condensate to facilitate injection through a coiled tubing rig into the bottom of the "open hole" section of the well at a depth of 2500 m. Approximately 0.4 wellbore volumes of diluted Solvent F was placed into the well over a period of about two hours to allow dissolution of scale in the wellbore and near-wellbore formation. Upon standing for 48 hours, the well regained temperature and was backflowed to a holding

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tank. Solvent returns were poor due to migration of chemical away from the wellbore through fractures deep in the injection formation below 2500 m, and displacement by brine from a nearby communicative injection well.

The well was again flushed with condensate to push the solvent deeper into the formation. The well was placed back into service for disposal of spent injection brine. Although the solvent apparently did not dissolve significant scale in the wellbore based on logging analyses, injection capacity improved. It is believed that the solvent dissolved significant scale in the permeable fractures over time and at the bottom hole temperature of > 100°C. The treated injection well successfully disposed of brine for many months after Solvent F treatment before requiring a mechanical cleanout.

CONCLUSIONS

Scale deposition from geothermal brines may include NORM as radium, thorium and lead. Commercially-available scale solvents were compared in laboratory dissolution tests with geothermal deposits containing radium co-deposited with barite. Distilled water, Salton Sea water, acids and bases dissolved very little barite or NORM. Scale solvents consisting of chelating agents and scale converters/surfactants dissolved significant amounts of scale and reduced NORM concentrations. The most efficient scale dissolver identified in the laboratory study successfully treated a geothermal injection well containing NORM scale resulting in an increase in brine disposal capacity. Scale dissolver treatment of geothermal wells appears to be cost competitive with mechanical methods. On the other hand, mechanical scale removal methods appear to be more cost effective in surface piping applications.

Minimization of NORM scales is best accomplished with inhibitors. However, when NORM deposits are formed, the results of this study indicate that they can be removed from piping and wells by scale dissolvers. The chelate-based dissolvers examined in this study are effective in solubilizing radium and thorium, especially at higher temperatures. Lead scales were not examined in this study, but the fact that the dissolvers solubilized other heavy metals, such as copper and iron, infers that they will be effective in chemically dissolving radioactive lead components from scale deposits.

ACKNOWLEDGMENTS

I thank UNOCAL Corporation management for permission to publish this paper.

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TABLE 1

Representative Salton Sea Brine Composition

pH ~ 5.5; Eh ~ -200 mV

Analyte	mg/kg		Analyte	mg/kg		Analyte	mg/kg
Ag	1		Mg	50		Br	80
As	10		Mn	760		Cl	129,000
B	300		Na	49,900		CO2	500
Ba	190		Pb	70		F	15
Ca	22,700		Rb	50		H2S	10
Cu	5		Sb	1		I	20
Fe	700		SiO2	480		NH3	380
K	12,300		Sr	380		SO4	100
Li	170		Zn	300		TDS	230,000

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TABLE 2

Analyses of Scales Used in Laboratory Studies

		Scale #1	Scale #2	Scale #3
Mineral Mode, wt%				
BaSO4		31.3	29.1	15
CaF2		3.2	61	1.2
Cu3As		<0.1	<0.1	52.8
FeO		9.2	2.4	11.7
SiO2, hydrated		54.6	7.1	17
Total		98.3	99.1	97.7
Radionuclide, Bq/g				
K-40		1	1.8	0.9
Ra-226		9.3	7.4	3.7
Ra-228		9	Not Analyzed	Not Analyzed
Th-232		2.4	2.7	1.9

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TABLE 4

Scale #2 Dissolution Results

		Scale Dissolution/Ra-226 Reduction, %		
Dissolver	Dissolver Type	23 C	60 C	100 C
A	Distilled Water (Control)	<1/<1	<1/<1	3/<1
B	25% Na4EDTA	8/11	31/10	41/6
C	25% NaOH	<1/<1	3/<1	3/1
D	25% HNO3	6/<1	5/<1	
E	High pH Chelate (EDTA?) with Surfactant	16/17	22/33	32/45
F	K5DTPA/Oxalate	10/20	10/68	71/75
G	30 wt% Solution of Blended Sequestrants	16/10	27/33	44/39
H	Chelate Blend; citric and carbazic acids?		5/9	
I	Chelate Blend; citric and carbazic acids?		8/22	
J	Chelate Blend; citric and carbazic acids?		7/21	
K	Chelate Blend with Surfactants		16/53	

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TABLE 3

Scale #1 Dissolution Results				
		Scale Dissolution/Ra-226 Reduction, %		
Dissolver	Dissolver Type	23 C	60 C	100 C
A	Distilled Water (Control)	<1/<1	<1/<1	2.1/<1
B	25% Na4EDTA	14/21	22/20	28/33
C	25% NaOH	9/4	17/7	34/5
D	25% HNO3	15/<1	20/2	
E	High pH Chelate (EDTA?) with Surfactant	16/17	22/33	32/45
F	K5DTPA/Oxalate	16/31	14/29	26/52
G	30 wt% Solution of Blended Sequestrants	13/12	17/14	17/19
H	Chelate Blend; citric and carbazic acids?		0/<1	
I	Chelate Blend; citric and carbazic acids?		4/3	
J	Chelate Blend; citric and carbazic acids?		7/6	
K	Chelate Blend with Surfactant		12/17	

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TABLE 5

Scale #3 Dissolution Results				
		Scale Dissolution/Ra-226 Reduction, %		
Dissolver	Dissolver Type	23 C	60 C	100 C
A	Distilled Water (Control)	<1/<1	<1/<1	<1/<1
B	25% Na4EDTA	20/15	32/30	35/50
C	25% NaOH	5/2	5/1	11/4
D	25% HNO3	51/6	56/4	
E	High pH Chelate (EDTA?) with Surfactant	29/14	18/28	30/41
F	K5DTPA/Oxalate	16/31	26/30	42/86
G	30 wt% Solution of Blended Sequestrants	23/17	17/14	39/40
H	Chelate Blend; citric and carbazic acids?		20/6	
I	Chelate Blend; citric and carbazic acids?		13/2	
J	Chelate Blend; citric and carbazic acids?		10/1.5	
K	Chelate Blend with Surfactant		13/25	

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FIGURE 1

SALTON SEA UNITS SIMPLIFIED FLOW SCHEMATIC

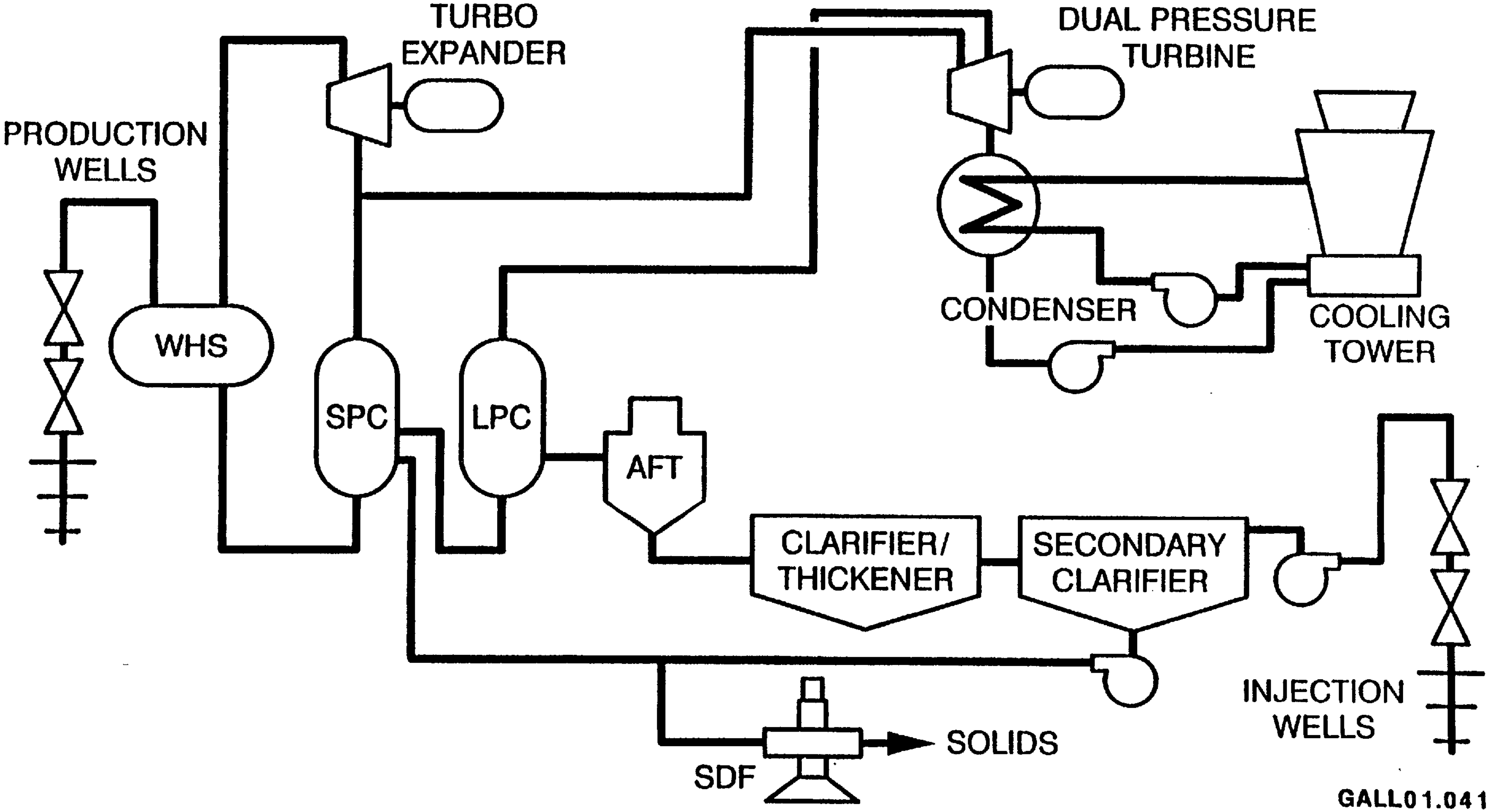

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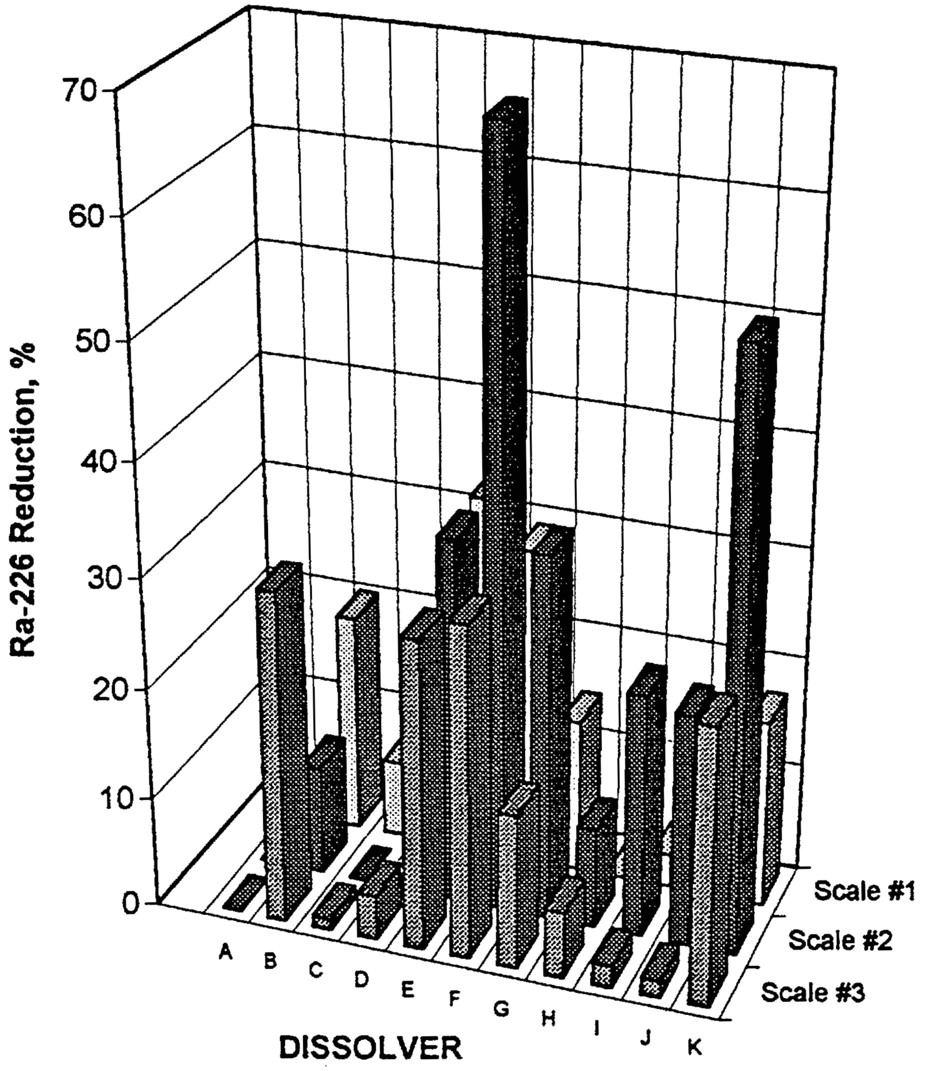
FIGURE 2

Ra-226 DISSOLUTION BY SCALE DISSOLVERS



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Remediation of Normally Occurring Radioactive Material (N.O.R.M.): A Field Trial

J.D. Orum, AMBAR Laboratories, D. Baudoin, AMBAR Laboratories, O. Briscoe, AMBAR, Inc.

Abstract

This paper describes a case history where 200 barrels of NORM contaminated sands and sludges were remediated to below regulatory limits and subsequently disposed as Non-hazardous Oilfield Waste (N.O.W.). The material treated initially registered as high as 180 pCi/gram of Radium 226. Upon completion of the remediation process, all materials were reduced to below 30 pCi/gram with some samples registering as low as 3 pCi/gram (background). The lower levels of radiation registered were a direct result of treating time. As a result of this process, no by-products were generated which fall under NORM regulated levels. The resulting data from this remediation of NORM waste were scrutinized by applicable regulatory agencies and found to be an acceptable method of remediation.

Introduction

Naturally Occurring Radioactive Material (N.O.R.M.) has become a significant issue for Regulatory Agencies and petroleum companies over the recent years. NORM will become an increasingly high visibility environmental issue, as it can be a health threat to both workers and potentially to the surrounding communities if not properly handled. Regulations have started in several states with federal agencies such as U.S. Environmental Protection Agency (EPA) to follow with additional regulations during the next few years. NORM is prevalent throughout the environment. It exists in soil, water, plants, petroleum, coal, lignite, phosphate, geothermal waste, waste water, humans and animals. Since humans can't smell, touch, see or feel NORM, a potential health threat could go undetected. NORM can only be detected and measured with special instruments(Ludlum Model 3 radiation detector). The radioactivity of NORM is due to the 'decay' process of specific atoms called radionuclides. This decay process yields radioactive particles, alpha and beta particles along with gamma radiation. This NORM radiation can be damaging to humans both on a long term and short term basis, **if the radiation is concentrated (contingent upon dose rate and exposure).**

The NORM radionuclides are uranium, potassium, radium, and radon. This falls under the category of Technology Enhanced Natural Radioactive Material (TENR). TENR is used to describe NORM waste resulting from various industrial activities that alter or concentrate NORM. Our primary interest is oilfield related NORM. This being concentrated due to scale buildup in well production tubing with often times considerable radioactive material. The associated production brine with gas or oil co-precipitates these radioactive materials along with $BaSO_4$, $CaSO_4$ et al. The primary concern is Ra 226 which has a half-life of 1,602 years.

Radium 226 produces a radiation field, alpha, beta particles and gamma radiation. Gamma radiation will easily penetrate the human body causing potential damage. Alpha and beta particles do not penetrate but can be washed from the skin. However, inhalation of the alpha and beta particles (or the airborne Ra^{226} particle) causes great concern. These particles accumulating in the respiratory tract which offers little resistance to radiation damage are the focus of regulatory efforts. Equally as important as Radium 226 is its gaseous daughter element, Radon 222 which can build up in confined spaces.

Radium 226 concentrations in the oilfield has been measured as high as 40,000 pCi/gram. When NORM is found it typically runs 155 pCi/gram. Estimates for the oilfield suggests 0.63 million metric tons of NORM are generated per year, a conservative estimate[1]. The Nuclear Regulatory Commission established under the Atomic Energy Act to address our atomic energy industry does not regulate radioactive material below 2,000 pCi/gram. It is acknowledged that health risks exist below 2,000 pCi/gram, thus states have filled the void most notably Louisiana (Louisiana Department of Environmental Quality - LADEQ). The LADEQ established a limit of 5 pCi/gram (laboratory activity level) for Ra 226 above background averaged over first 15 cm of soil. This has now been changed to 25 micro Roentgens/hour (exposure level) or twice the background reading whichever is lower, to

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facilitate field surveys (Ludlum Radiation Meter) as pCi/gram can only be measured in the laboratory. The distinction between NORM and Non-hazardous Oilfield Waste (NOW) is set at 30 pCi/gram with NOW being less than the 30 pCi/gram. This value is important as it is the value for proper disposal in Louisiana. The LADEQ has estimated over 20,000 NORM sites in Louisiana. The EPA regulation for Radium 226 in Drinking Water is 5 pCi/liter[2] which although not a direct concern aids in quantification[2] (Table 1).

Radon 222 has a short half-life of 3.8 days but leaves radioactive lead (Pb 210) with a half life of 22 years. As Radon gas can be produced with methane (CH4) a Pb 210 layer will often be left in piping and equipment. However, Radon's primary health concern is due to it gaseous, intrusive nature accumulating in houses and ground water. The EPA recommends less than 4 pCi/liter on an annual basis for confined spaces and 300 pCi/liter for drinking water[2] (Table 1).

As stated earlier our primary concern is NORM in the oilfield caused by scales and their subsequent removal and disposal. NORM scales are co-precipitated Ra 226 with Barium, Calcium and other Group II alkaline earth elements as sulfates and carbonates. This scale adheres to well production tubing and surface equipment creating a NORM concentration. To better understand the remediation process used in this paper, an overview of existing disposal techniques is in order. The disposal options are as follows:

Minimization. The NORM material is removed from tubing and vessels since the regulated material is usually approximately 30% of the actual volume. Various procedures are used to concentrate the NORM material. This in turn raises the radiation readings. The alternative for disposal of this concentrated NORM is government approved burial sites in Utah or Washington. This is quite expensive and alive with liability issues.

Encapsulation. The concentrated NORM material could be enclosed in a hardened chemical plug and placed in a plug and abandoned well. The 1600 year half-life of Ra 226 and 50 year life of the well casing makes this not a permanent solution to the disposal problem. This is less expensive than other alternatives and is used by petroleum companies but has associated liability issues.

Slurry and Downhole Injection. The NORM materials are finely ground and blended with a viscous fluid. This slurry is injected into the wellbore. The liability issues are significant with this approach as water aquifers are vulnerable if the material migrates.

Land Farming. This uses specifically state approved land areas and low levels of radiation. (less than 30 pCi/gram). This is accomplished through surface dilution of the contaminated material with non-contaminated material to achieve an activity level less than 5 pCi/gm. The liability issue does not escape this approach.

The remediation process used in this field trial utilized dissolution chemistries and solids handling equipment. Conceptually this process took the NORM material mixed it with a proprietary chemistry. This chemistry dissolved the scale containing the radioactive species usually Ra 226 (along with Ba, Ca and other alkaline earth metals) leaving behind NOW solids. The liquid would then be injected into Class II salt water injection well(s) and the non-radioactive solids (NOW) would go to a licensed NOW facility. The liability issues are non-existent with this dissolution process.

Theory

The remediation (or dissolution) process consisted of two separate and distinct parts. The first part being the chemistries used to dissolve the radioactive species i.e. Ra 226 leaving solids and liquid that can be readily disposed as NOW wastes. The second part being the equipment and procedures.

The first part or dissolution process employed unique proprietary chelation chemistries. The most common oilfield scale dissolution chemistries are the inorganic acids such as Hydrochloric (HCL) and Hydrofluoric (HF) to dissolve oilfield scales such $CaCO_3$ (Calcite) and $CaMgCO_3$ (dolomite). It is common knowledge that certain scales most notably $BaSO_4$ is not acid soluble and is in fact quite insoluble. NORM during its formation co-precipitates Ra 226 with $BaSO_4$ requiring removal by means other than acid. A dissolution process using various chelants was used successfully.

A brief overview of chelation theory is needed. To understand chelation, one needs to understand the nature and behavior of metal ions such as Ca^{++}, Ba^{++}, Ra^{++} (Group II alkaline earth elements). The metal ions (Ca^{++}, Ba^{++}, Ra^{++}) exhibit a positive charge when a metallic compound is dissolved in water. These metal ions surround themselves with negative ions. The number of negative ions that surround or coordinate with the metal ions is usually 4 or 6. The centers of coordination or reactive sites are responsible for various reactions including chelation[3].

In an aqueous solution which is normally the case, these reactive or coordination sites are occupied by water molecules. However, when chelants are present which more strongly compete for these *sites* than water molecules the resulting ion takes on new properties. One of these being increased solubility (Fig. 1). Thus a formal definition of chelation is an equilibrium reaction between a metal ion and a complexing agent, characterized by the formation of more than one bond between the metal and a molecule of the complexing agent and resulting in the formation of a ring structure incorporating the metal ion[4,5].

Process

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The second part of the remediation process being the equipment and procedures used with the dissolution chemistries:

Equipment Overview (Fig. 2). The equipment was comprised of a 'closed loop system' into which NORM material was placed using water to make a 'slurry' of the NORM sands & sludge. This 'slurry'. was pumped over a 'solids shaker'. The shaker physically separated the slurry by allowing the fluids (water) to percolate through the screens while the solids were conveyed across the shaker and deposited into a loading hopper. From here the solids were conveyed via an auger to the Dissolution Tank ('DT") containing preheated Dissolution chemistries. (Dissolution chemistries were preheated in 'Heater Tank' to 185°F). This was mixed and circulated until radioactive scale was removed from the solids. At this point the contents were run over a 'process shaker' which separated the solids and liquids as NOW wastes. The fluids returned to the heater tank and the solids were deposited into containers for shipment to disposal.

Procedure Overview. Prior to processing a container(s) of NORM material, a Radiation Safety Officer (RSO) conducted extensive safety precautions for workers and the work area. In order to depict how this was done a typical step-by-step procedure is given:

- State regulatory agency approval obtained
- Baseline radiological survey conducted at job site prior to start-up
- Radiation Safety Officer (RSO) ensured proper worker training and safety equipment present.
- RSO marks off job site as 'Caution: Radioactive Material, Restricted Area
- Prior to each day processing, RSO completed 'Radiation Work Permit'.

This included work activities, work assignments, contamination & radiation levels, area postings, emergency procedures, & respiratory protection.

- Personnel exiting received foot and hand frisk. At end of day workers perform whole body frisk.
- No equipment was removed from area that showed twice background readings.
- Twice daily radiation and contamination surveys were posted at Restricted Area boundary. (micro Roentgen/hr... Ludlum meter readings).
- During the Dissolution process air sampling was performed by RSO in Restricted Area and in the worker's breathing zone.
- A representative sample of each batch of NORM material was taken before and after the dissolution process. These samples went to a 3rd party radiological lab approved by the National Bureau of Standards for radio analyses (pCi/gram readings). Thus as each batch of NORM material was processed, attention to 'safety' was paramount. The determination as to when a NORM batch was processed was by meter readings of less than 20 micro Roentgens/hr for a 1 liter sample. Again the samples were sent to a 3rd party radiological lab to confirm the less than 30 pCi/gram value to be classified as NOW waste[6,7].

Data and Results

The fourteen batches (200 barrels) of NORM material were processed over a twelve day time frame. The data in micro Roentgens/hr per 1 liter (Ludlum 3 meter) samples reflect significant reductions in radiation readings (Fig. 3). The percent reductions ranged from 75% to 85% over all fourteen batches.

Radiological lab analysis (pCi/gram) confirmed the micro Roentgens/hr per 1 liter data as would be expected (Fig. 4). All pCi/gram determinations were significantly reduced from the original samples by 75% to 95%.

The exposure times for each of the fourteen batches ranged from 1.0 to 3.0 hours in the "Dissolution Tank". From the Ludlum 3 radiation meter readings (micro Roentgens/hr), this proved to be adequate to achieve the desired 20 micro Roentgen/hr reading.

All but 2 batches were less than the 30 pCi/gram level to be classified as NOW waste. These 2 batches labeled gbd16 and gb24, gave the highest initial readings of 128 and 147 pCi/gram, respectively (Fig. 4). These two batches were blended with batches , gbb3 and bgg7. This is an accepted procedure, repackaging, so as to achieve less than 30 pCi/gram necessary for NOW waste classification. An increase in dissolution time from 2 hours to 4 hours would certainly have yielded these batches as NOW waste.

Conclusions

As field operations progress with this Dissolution Remediation Process, a better correlation of dissolution time and radiation reduction will ensue. The variables of scale type, amounts, and amorphous components all affect this process. Empirical observations along with more in-depth lab work will allow us to quantify these variables. This field trial showed the following:

- Radioactive scale can be removed from sand using this Dissolution Process
- NORM solids can be disposed as NOW wastes via this Dissolution Process

Acknowledgments

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Nomenclature

pCi/gram = pico Curie per gram
uR/hour = micro Roentgens per hour
pCi/liter = pico Curie per liter

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Radionuclide Contaminant	PQL (pCi/liter)
^{226}Radium	5
^{228}Radium	5
(natural) Uranium	5
^{222}Radon	300
Gross alpha emitters	15
Gross beta emitters	30
Radioactive cesium ^{134}	10
Radioactive cesium ^{137}	10
Radioactive iodine	20
Radioactive strontium ^{89}	10
Radioactive strontium ^{90}	10
Tritium	1,200

Table 1. Practical Quantitation Levels (PQL) for radionuclide contaminants.[2]

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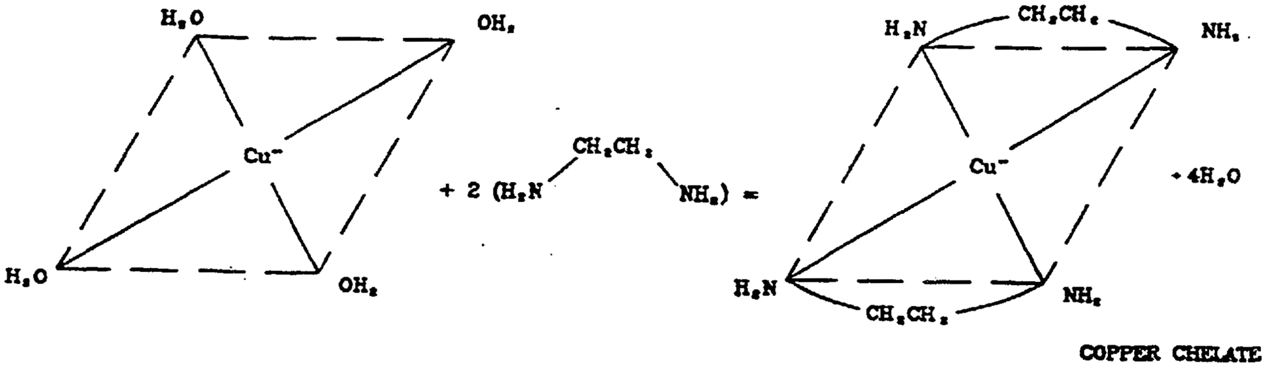

Figure 1: Reaction of Aqueous Copper Ions with Ethylenediamine

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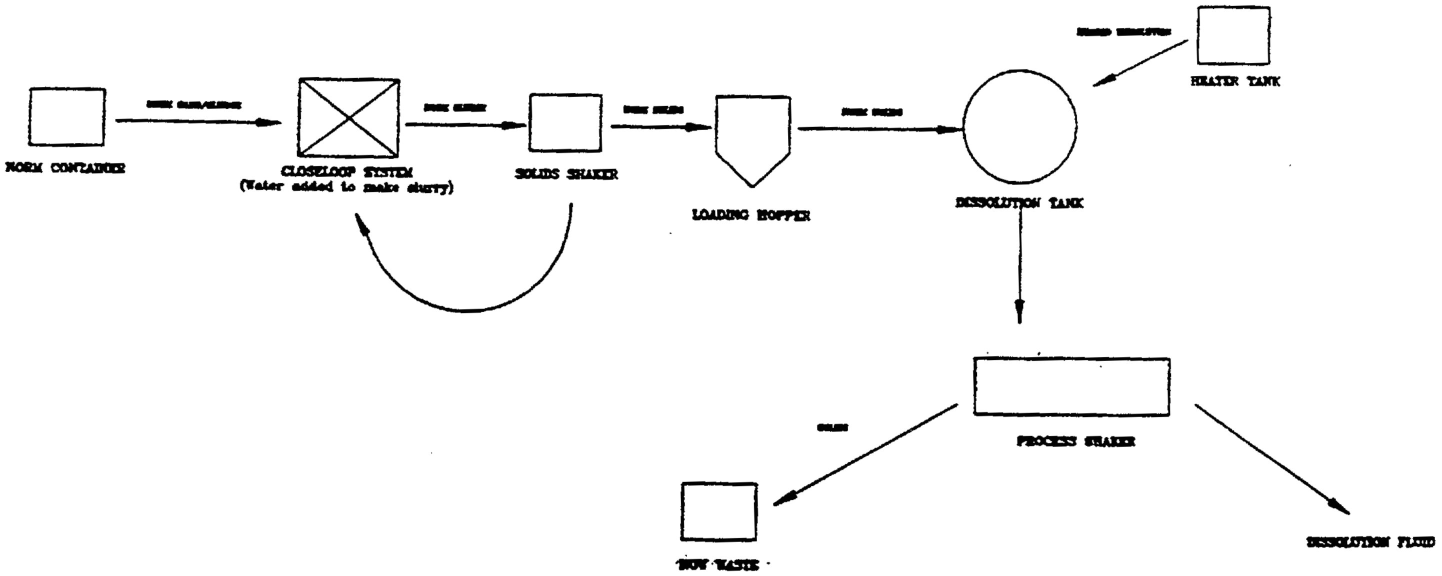

Figure 2: Dissolution Remediation Process / Equipment Overview

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Process Order # vs. uR/hr - 1 liter

Dissolution Remediation Test

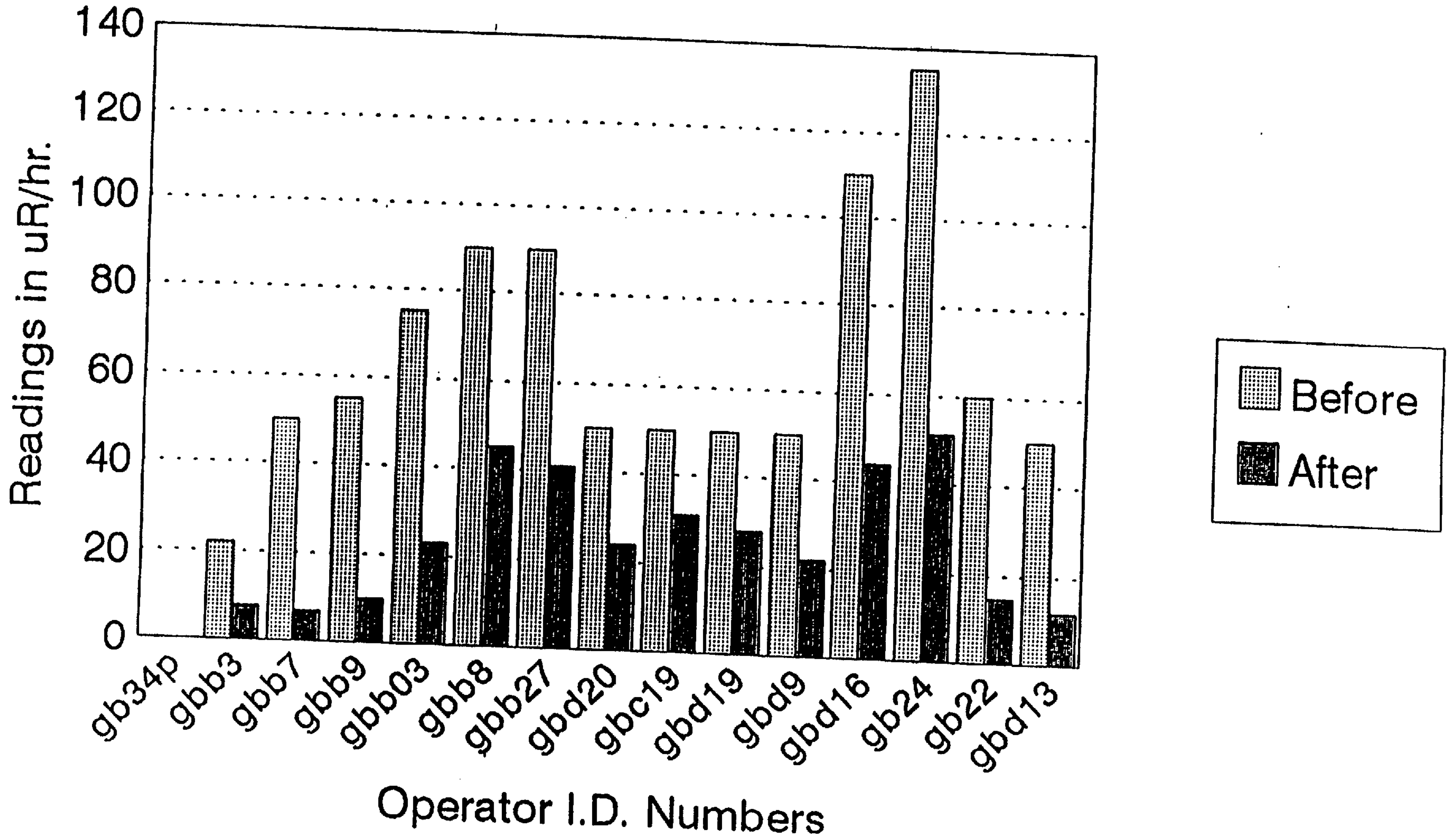

Fig.3

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Process Order # vs. Ra-226

Dissolution Remediation Test

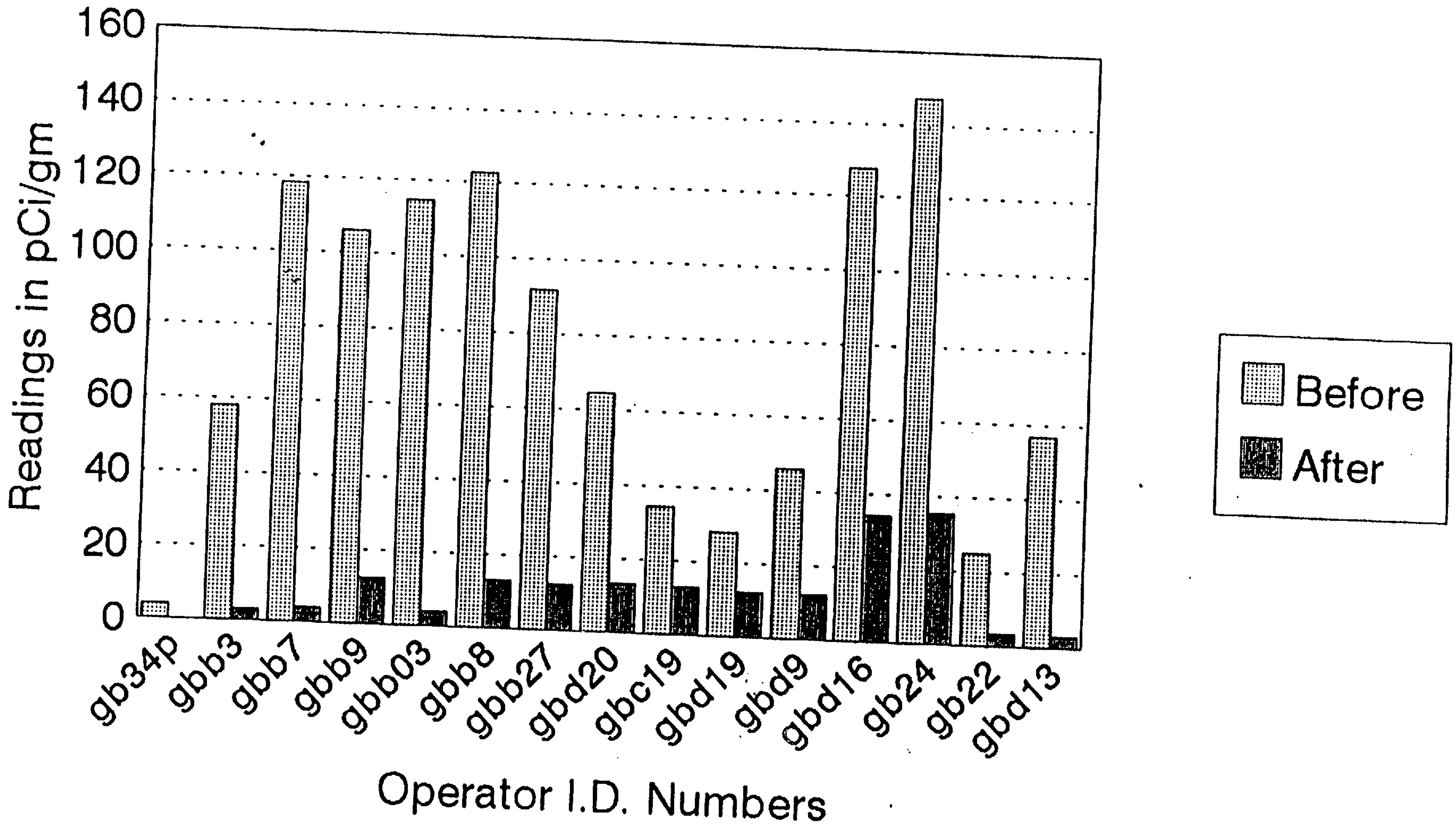

Fig.4

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Computer Aided Prediction of NORM Associated Scale

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Summary. When predicting the formation and growth of NORM (Naturally Occurring Radioactive Material) scale using chemical simulation models, several items must be known to a high degree of accuracy. These include: 1) the mathematical expressions used to calculate NORM co-precipitation; 2) the activity coefficient values of the $RaSO_4$ and $BaSO_4$ species in the solid solutions; 3) the activity coefficient values of the aqueous solutes, often at high ionic strengths, pressures, and temperatures; and 4) the values of the standard state thermodynamic properties at the specified temperatures and pressures.

In this paper, the underlying theory used to generate values for these parameters, the chemical model used to calculate the co-precipitation of Ra in $BaSO_4$, and the application of chemical models to scale problems is discussed.

Introduction

Computer-based, chemical simulation models are valuable tools in predicting a variety of chemical conditions, such as solubility, corrosion, reaction yields, and in some cases, reaction rates. Chemical simulation models are especially useful when the chemical process in question is either difficult to determine experimentally, or requires significant laboratory costs.

The quantification of NORM scaling in oil and gas associated brine production systems is an example of a task that can be assisted by chemical simulation models. This is because, NORM scale, which exists in a variety of brines is time consuming to reproduce experimentally, and the handling of radioactive material in laboratories is regulated by the government.

NORM in its literal sense, includes the complete list of radioactive isotopes that are found in scales and sludges associated with energy production. The origin of the radioactive isotopes in producing formations has been discussed elsewhere (Gray, 1993; Smith, 1987), and the occurrence of NORM scale in production equipment has been reported (Oddo et al., 1992). Radium (^{226}Ra, atomic weight=226) represents the most common of the NORM components, partly due to its long radioactive half-life (1600 yr). Thus, in NORM scale, radium is the principal component investigated.

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Radium concentrations in the brine are exceedingly low. For example, they have been observed in north Texas brines at concentrations between 1.12 and 4.65 10^{-12} molal (moles/kg H_2O), (Langmuir and Melchior, 1985). As a result, pure $RaSO_4$ is extremely difficult to form. For example, the reported solubility product constant of $RaSO_4$ ($Ksp_{(RaSO_4)}$), is $10^{-10.37}$ (Smith and Martel, 1976). At an aqueous concentration of 10^{-12} M, the SO_4 concentration required to precipitate $RaSO_4$ would necessarily be above $10^{1.63}$ or 42.7 M.
By comparison, barium concentrations in brines are often between 10^{-6} and 10^{-3} M, and although its solubility is only slightly higher than $RaSO_4$ ($Ksp_{(BaSO_4)}=10^{-9.96}$), sulfate concentrations required to precipitate barite are between 10^{-3} to 10^{-6} M.

Formation of NORM scale occurs when Ra substitutes for Ba in barite scale, producing a co-precipitated $(Ba,Ra)SO_4$ scale. The ability of Ra to substitute is due to similarity in ionic radius and coordination of the two elements (Langmuir and Riese, 1985). The amount of substitution is often small, due to the higher abundance of barium in solution versus radium.

Church (1977), observed Ra/Ba contents in modern marine barites of 2.4×10^{-10} g Ra/g Ba, or one atom Ra per 7.14 trillion atoms of Ba. When this value is converted to radiation units, one kilogram of equivalent barite scale would produce 1.886×10^{6} disintegrations per second (dps) each producing one unit of γ-radiation.

As an example, the mass of barite (4.45 sg) in a 1 ft section of 3 inch I.D. pipe with one inch scale, is 13.75 kg. From this mass, 2.5925×10^{7} dps occur. If a 70 kg individual is handling this section of pipe, the maximum radiation dosage absorbed (assuming contact with the full area of pipe and 100% body absorbance of γ-radiation), would be:

$$\frac{2.5925x10^{7}\ \gamma decays}{s} * \frac{0.26 MeV}{\gamma decays} * \frac{1.6x10^{-13} J}{MeV} * \frac{10^{2} \gamma rad\ kg}{J} * \frac{1\ rem}{\gamma rad} * \frac{1}{70 kg} \tag{1}$$

$$=1.54x10^{-6}\frac{rem}{s} = 5547\frac{\mu rem}{hour}$$

where 0.26 (MeV/γ decay) is the energy of the γ-ray photon (Handbook of Chemistry and Physics, 1979. pg. B-410), and 1.6×10^{-13} (J/MeV), 10^{2} (γ-rad kg/J) and 1 (rem/γ-rad) are conversion factors. As a comparison, Oddo et al. (1992), reported NORM dosages ranging between 50- 4000 μrem/hr at fifteen locations along a production system in the Antrim Play, Michigan. Ten readings were between 150 and 1000 μrem/hr. Smith (1987) reported surface dose rates of 12,000 μrem/hr on external scale deposits of production tubulars.

The extent to which Ra co-precipitation occurs, and the ability of scientists to predict and prevent its formation, depends upon how well we understand the chemical mechanisms and how well we can model the process.

In the current study, development of the equations necessary to predict the formation of NORM scale is presented. The general solubility theory, and how it is modified to include radium co-precipitation is shown. Following this, determination of the parameters and variables needed to calculate radium co-precipitation is discussed. The mathematical model is then used to predict precipitation of NORM scale under laboratory and field conditions. The final section of this paper presents an application of the model in NORM remediation.

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MODEL DEVELOPMENT

When developing a reaction for a new chemical simulation or adding one to a current program, the first step in the process is to develop the mathematical relationship. In this section, the development of the co-precipitation model which describes NORM scaling is presented.

The co-precipitation of $(Ra,Ba)SO_4$ is described by the following stoichiometric reaction:

$$BaSO_4(barite)+Ra^{+2} \rightarrow RaSO_4(barite)+Ba^{2+} \qquad (2)$$

where the $RaSO_4$ solid species exists within the $BaSO_4$ (barite) crystal structure. This phenomenon is commonly referred to as a solid-solution reaction. The energy to form *$RaSO_4$ in a Barite crystal* differs from the reaction energy forming *pure $RaSO_4$*. From this energy, the abundance of radium in the barite lattice can be calculated. This is determined through the following series of equations.

Energy is released when pure $BaSO_4$ and $RaSO_4$ precipitate independently, according to the reactions:

$$M^{2+}(aq)+SO_4^{2-}(aq) \rightarrow MSO_4(barite)$$

$$\Delta G_r^{\circ}(M{=}Barium)=-13.6\frac{kcal}{mole} \qquad (3)$$

$$\Delta G_r^{\circ}(M{=}Radium)=-14.16\frac{kcal}{mole}$$

where ΔG_r° is the Standard Free Energy of the precipitation reactions, and MSO_4 (barite) is the $BaSO_4$ and $RaSO_4$ precipitate which forms within a barite lattice. From this, the solubility of Radium and Barium is calculated:

$$K_{sp}=\frac{\{Ba^{2+}(aq)\}\{SO_4^{2-}(aq)\}}{\{BaSO_4(barite)\}} =\exp^{-\frac{\Delta G_r^{\circ}}{RT}}=10^{-9.96}$$

$$K_{sp}=\frac{\{Ra^{2+}(aq)\}\{SO_4^{2-}(aq)\}}{\{RaSO_4(barite)\}} =\exp^{-\frac{\Delta G_r^{\circ}}{RT}}=10^{-10.51} \qquad (4)$$

where K_{sp} is the solubility product constant for the reaction, and the bracketed terms are the activities of the aqueous and solid species.

The activity of the aqueous species is further defined (generalized for barium):

$$\{Ba^{2+}\}=M_{Ba^{2+}}*\gamma_{Ba^{2+}} \qquad (5)$$

where M_{Ba2+} is the concentration of the Ba^{2+} species (moles/liter) and γ_{Ba2+} is the activity coefficient of the Ba^{+2} species in solution. The latter term takes into consideration the effects of the brine composition on the species.

The activity of the solid species can also be re-defined:

$$\{BaSO_4(cr)\}=X_{BaSO_4(cr)}*\lambda_{BaSO_4(cr)} \qquad (6)$$

where $X_{BaSO4\,(cr)}$ is the $BaSO_4$ mole fraction of the crystal (X_{BaSO4}=1 for pure barite) and $\lambda_{BaSO4\,(cr)}$ is the activity coefficient of the $BaSO_4$ solid species ($\lambda_{BaSO4\,(cr)}$ =1 when $X_{BaSO4\,(cr)}$ =1, i.e., in pure barite).

The equilibrium (Mass Action) expression for equation (2) is written and expanded using equations (4), (5), and (6):

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$$K=\frac{\{RaSO_4(barite)\}}{\{BaSO_4(barite)\}}*\frac{\{Ba^{2+}(aq)\}}{\{Ra^{2+}(aq)\}}$$

$$=\frac{X_{RaSO_4(barite)}}{X_{BaSO_4(barite)}}*\frac{\lambda_{RaSO_4(barite)}}{\lambda_{BaSO_4(barite)}} \qquad (7)$$

$$*\frac{M_{Ba^{2+}(aq)}}{M_{Ra^{2+}(aq)}}*\frac{\gamma_{Ba^{2+}(aq)}}{\gamma_{Ra^{2+}(aq)}}$$

and

$$K=\exp\frac{-\Delta G_r^o}{RT} \qquad (8)$$

$$G_r^o=\Delta G^o_{f,RaSO_4(barite)}+\Delta G^o_{f,Ba^{2+}(aq)} -\Delta G^o_{f,BaSO_4(barite)}-\Delta G^o_{f,Ra^{2+}(aq)}$$

where K is the equilibrium distribution constant of radium in barite. In the exponential term, the numerator represents the energy released (absorbed) by the reaction, R is the universal gas constant (1.987 cal/mol K), and T is temperature (Kelvin).

The experimentally measured quantities (e.g. concentrations and mole fraction) in equation (7) can be separated from the computer generated quantities (e.g. constants) to produce:

$$K*\frac{\lambda_{BaSO_4(barite)}}{\lambda_{RaSO_4(barite)}}*\frac{\gamma_{Ra^{2+}(aq)}}{\gamma_{Ba^{2+}(aq)}} \qquad (9)$$

$$=\frac{X_{RaSO_4(barite)}}{X_{BaSO_4(barite)}}*\frac{M_{Ba^{2+}(aq)}}{M_{Ra^{2+}(aq)}}$$

Defining D as the distribution coefficient, and setting it equal to the calculated values on the left hand side, we produce the "Berthelot-Nernst" or "Henderson-Kracek" Distribution Law (McIntyre, 1963).

$$D=\frac{X_{RaSO_4(barite)}}{X_{BaSO_4(barite)}}*\frac{M_{Ba^{2+}(aq)}}{M_{Ra^{2+}(aq)}} \qquad (10)$$

Modeling the Left-Hand-Side of Equation (9).

Once the generalized model has been developed, the procedure in which each constant (or parameter) in the model is calculated must be addressed. In the current model, terms on the left hand side of equation (9) are the constants to be determined.

Determination of K. The calculated values of K can be determined from equation (8), once the values of ΔG^o_r have been obtained. The values in equation (8) that are used to calculate ΔG^o_r are provided in Table 1. A value of $\Delta G^o_{f,BaSO4(barite)}=-325,563$ cal/mol, taken from Helgeson et al. (1978), was chosen because it was consistent with the solubility measurements of Blount (1978), and with the values of $\Delta G^o_{f,Ba2+}$ and $\Delta G^o_{f,SO42-}$ (Shock and Helgeson, 1988) .

The value for $\Delta G^o_{f,RaSO4(barite)}$ was calculated using the Linear Free Energy correlation developed by Sverjensky and Molling (1992). In this approach, the effect of the barite lattice on $RaSO_4$ precipitation is considered. A value of $\Delta G^o_{f,RaSO4(barite)}=-326,290$ cal/mol was calculated.

Based upon these values, K=2.56 at 25°C and 1 atm.

Since the values provided in Table 1 vary with temperature and pressure, the simulation model must also include a set of equations to account for this. The equations

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suggested are the Helgeson Equations of State, because they cover a wide range of temperatures and pressures (Rafal et al., 1994).

Determination of solid activity coefficients (*λ_{BaSO4} and λ_{RaSO4}*). The value of $\lambda_{RaSO4\,(barite)}$ is determined using Regular Solution Theory (Garrels and Christ, pp. 44-47), in which the value of λ_{RaSO4} is curve fitted to experimental data using a one parameter regular solution equation:

$$\log_{10}\lambda_{RaSO_4(barite)} = \frac{B}{2.303RT} * X^2_{BaSO_4(barite)} \quad (11)$$

where B is a constant, independent of composition, and calculated from a curve fitting procedure. The empirical value obtained for B is 210 cal/mol, and is used to calculate both λ_{RaSO4} and λ_{BaSO4}. Thus, for example, at X_{BaSO4}=0.95 (X_{RaSO4}=0.05), $\lambda_{RaSO4(barite)}$ (70°C)= 1.32 and $\lambda_{BaSO4(barite)}$ (70°C)=1.001.

The ratio of the two activities coefficients in equation (9) can be rearranged to produce:

$$\frac{\lambda_{BaSO_4(barite)}}{\lambda_{RaSO_4(barite)}} = 10^{\frac{45.89}{T} * (1-2*X_{BaSO_4(barite)})} \quad (12)$$

which is now only a function of $X_{BaSO4(barite)}$.

Determination of aqueous activity coefficients (*γ_{Ba2+}, γ_{Ra2+}*). Calculation of γ_{Ba2+} and γ_{Ra2+} involves a rigorous mathematical derivation which is beyond the scope of this text. There are several mathematical models available to calculate aqueous activity coefficients, and most chemical simulation programs incorporate one or more of the models. However only a few are accurate at the ionic strength observed in produced brines. Therefore, when selecting a chemical simulation program, one should be aware of the range of temperatures, pressures and ionic strengths over which the model is accurate.

The mathematical models which provide γ_{Ba2+} and γ_{Ra2+} values over a broad range of chemical conditions include, the Bromley, Pitzer, and Chen activity coefficient models. The derivation of these models and their performance in various ionic solutions can be found elsewhere (Zemaitis et al., 1986, Chapter IV). In this work, the Bromley-Zemaitis model supplemented with the Meissner family of curves, is used to calculate γ_{Ba2+} and γ_{Ra2+} (Rafal and Sanders, 1995). This treatment has led to a predictive model with broad application over the range (T=0 to 300°C, P=0 to 1 Kbar, and ionic strength=0 to 30 molal).

Modeling the Right Hand side of Equation (9).

In order to predict the formation of NORM containing barite scale, two of the variables on the right-hand side of equation (9) must be known explicitly. When no analytical data is available, a hypothetical case or scenario can be run.

Determination of X_{BaSO4} and X_{RaSO4} (Mole fractions of $BaSO_4$ and $RaSO_4$ in the scale). The mole fraction of $BaSO_4$ and $RaSO_4$ has the following relationship:

$$X_{RaSO_4(barite)} + X_{BaSO_4(barite)} = 1 \quad (13)$$

Experimentally, *X_{BaSO4} and X_{RaSO4}* can be obtained by digestion of the scale and measuring Ba, Sr, Ra (cations), and SO_4 (anions). Alternatively, the amount of radium in the solid can be quantified by measuring the amount of radioactivity in a known mass of solid.

If *X_{BaSO4} and X_{RaSO4}* are to be computed, then

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concentrations of barium and radium in solution must be determined experimentally or entered as hypothetical values.

Determination of Ba and Ra solution concentrations (M_{Ba} and M_{Ra}). The values of M_{Ba} and M_{Ra} are determined either experimentally or computed from known mole fraction values (X_{BaSO4} and X_{RaSO4}). When total barium and radium concentrations are obtained experimentally, Ba^{+2} and Ra^{+2} concentrations can be back-calculated using the mass balance equations.

$$Ba(total) = Ba^{2+}(aq) + BaOH^{-}(aq) + Ba(OH)_2(aq) + BaSO_4(aq) \tag{14}$$

and

$$Ra(total) = Ra^{2+}(aq) + RaOH^{-}(aq) + Ra(OH)_2(aq) + RaSO_4(aq) \tag{15}$$

where the left hand side represents the measured concentration of barium and radium in solution, and the right hand side represents the concentration of each barium and radium containing species in the solution. The two above equations can be rearranged and combined with the equilibrium equations for each species to solve for the concentration of free Ba^{+2} and Ra^{+2} in solution. This is done by rewriting equation (14) and (15) as:

$$\begin{aligned} M_{Ba^{2+}} &= \alpha_{Ba^{2+}} * Ba(total) \\ M_{Ra^{2+}} &= \alpha_{Ra^{2+}} * Ra(total) \end{aligned} \tag{16}$$

where α_{Ba2+} and α_{Ra2+} represent the fraction of total barium and radium that is in the Ba^{2+} and Ra^{2+} species. The values of α_{Ba2+} and α_{Ra2+} are calculated by the chemical simulation program.

Equation (9) can now be rearranged to produce the final form for calculating co-precipitation.

$$2.56 * 10^{\frac{45.89}{T} * (1 - 2 * X_{BaSO_4(barite)})} * \frac{\gamma_{Ra^{2+}}}{\gamma_{Ba^{2+}}} = \left(\frac{1}{X_{BaSO_4(barite)}} - 1\right) * \frac{\alpha_{Ba^{2+}} * Ba(total)}{\alpha_{Ra^{2+}} * Ra(total)} \tag{17}$$

In this final form, either $X_{BaSO4(barite)}$ or the measured barium and radium concentrations must be known. The remaining values are calculated by the computer, provided the appropriate mathematical expressions are incorporated into the computer program.

Selection of a Chemical Simulation Software

A variety of public and private computer codes are available to the user. Each code may vary in the way the constants (e.g. K and γ) are calculated. In the current work, the program ESP[1] was used. This program incorporates the theoretical models and equations discussed above, and incorporates the co-precipitation reaction into the solubility calculations.

Comparing the Predicted Values of Constants to Experimental Data

Before NORM scale predictions can be performed, the chemical simulation model must first be evaluated with experimental data. In the following section, the current model is evaluated with respect to how accurately it predicts values of the constants on the left hand side of equation (9), and also simple solubility experiments. This tasks helps to increase the users confidence in the

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simulation tool.

Activity coefficient calculations. The accuracy of activity coefficient calculations is important in predicting NORM scale formation and solubility. Thus, it is important that when using a computer model, that the software selected contains the equations necessary to calculate these values accurately.

Figure 1 is a plot of the simulated and reported mean activity coefficients for $BaCl_2$ in water over five ranges of salinities. It can be seen the current chemical simulation program using the Bromley-Zematis model discussed above, produces good prediction of the data throughout the concentration range.

Currently, experimental data for radium is not available, and therefore the activity coefficient values must be estimated. However, interaction parameters for Ra^{2+} are assumed to be the same as for Ca^{2+} (cf. Langmuir and Melchior, 1985 used the same assumption while using the Pitzer method to calculate activity coefficients), and so reasonable estimation values are available.

Solubility vs temperature values. As mentioned previously, the values in Table 1, and therefore K_{sp} and K vary with temperature and pressure. Figure 2 is a plot of the temperature dependent solubility product constant ($pK_{sp}= -\log(K_{sp})$) for $RaSO_4$ (Langmuir and Melchior, 1985) and $BaSO_4$. Also plotted is the computer simulation of these values. It can be seen that without corrections for temperature and pressure, the value used in the calculations may be off by a factor of 10 or more. In this simulation, good agreement exists between the calculated and predicted values, especially at higher temperatures.

The ability to accurately predict the solubility of $BaSO_4$ under various temperatures, pressures, and ionic strengths, is paramount to NORM calculation, since barite is the primary scale formed. Figure 3 is a plot of the solubility of barite at varying temperatures, pressures and ionic strength. The solubility varies considerably, as would be expected from the plots in Figures 1 and 2.

$RaSO_4$ solubility data. As with $BaSO_4$, the simulation model was compared to reported solubility data for $RaSO_4$ (Nikitin and Tolmatscheff, 1933). These results are shown in Figure 4. The experiments were performed at 20°C and 0 molal ionic strength, and were considered the most careful and thorough study of $RaSO_4$ solubility in aqueous solutions (Langmuir and Riese, 1985). It can be seen that good prediction was obtained over the range of the experimental data.

Prediction of Published NORM Co-precipitation data

Reliable data on the $BaSO_4$-$RaSO_4$ co-precipitation is sparse, and only a handful of references were observed in the chemical abstracts between the years 1914 and 1995. The experiments carried out by Doerner and Hoskins (1925) were selected to evaluate the performance of the chemical model.

Results of the simulation are presented in Table 2, along with data from the referenced work. The first column in Table 2 identifies the experimental results extracted. The experiments carried out by these authors varied by the method of precipitation. The first five experiments (identified as Table IV-A) represented a rapid precipitation reaction with no agitation. The second four (identified as Table IV-B) represented a slow precipitation reaction at elevated temperatures (not provided) and rapid agitation. The last three (Table IV-C) represented precipitation by evaporation.

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As seen in the table, there is good agreement between the experimental and simulated results in column sets 1, 2, and 3, despite the variations in precipitation method, solution chemistry, and reaction temperature.

The last set of columns represents the fraction of NORM in the barite, and are plotted in Figure 5. These value are directly related to the radioactivity of a given mass of solid. The total error ranged between 2.7 and 33.7 %, with an average of 10.8 %. This means that a fairly accurate prediction of the scale radioactivity can be made from the simulation.

Prediction of NORM scale in production tubing

Simulation of NORM scaling is presented in Figures 6 through 8. In this simulation, the well depth was 14,000 ft, the bottom hole pressure was 700 atm, and bottom hole temperature was 150°C. Also, the well temperature and pressure was assumed to increase linearly with depth. The simulated brine contained $1x10^{-12}$ M total radium, $1x10^{-4}$ M total barium, and was in equilibrium with barite at the formation depth (14,000 ft).

Figure 6 is a plot of the total barium and radium concentration as a function of depth. The concentration of barium and radium dropped continuously as the brine flowed up the pipe. Nearly 96% of the barium and 80 % radium were calculated to precipitate out on the tubing. Figure 7 is a plot of the simulated mass of scale produced in each section of pipe per 1,000 barrels of brine produced. In this simulation, there was one major area of scaling. This occurred at the bottom of the well, between 12,000-14,000 ft.

The ratio of $BaSO_4$ and $RaSO_4$ mass also varied with depth, suggesting that the radioactivity of the scale will vary with conditions. This variation is illustrated in Figure 8, where the relative radiation dosage of the scale was plotted against tubing depth. It can be seen that the scale at the surface was nearly five times as radioactive as the scale in the bottom of the pipe.

Simulation of NORM Scale Dissolvers

Chemical simulation programs can also be used as a tool in place of laboratory work to study approaches in removing NORM. In this simulation, the predicted efficiency of NORM scale dissolvers was calculated.

Figure 9 is a plot of the simulated performance of various scale dissolvers. In this plot 234 g/l of NORM containing barite was dissolved with various formulations of scale dissolvers available to the industry (Paul and Fielder, 1992; Paul, 1994). To this solution, additions of K_2CO_3 and Na_2CO_3 were simulated. In some simulations, 1 mole of EDTA (ethylenediamine tetraacetic acid), DTPA (diethylenetriamine pentaacetic acid), and oxalic acid were added.

The percentage of the sulfate scale that was dissolved or converted to carbonate varied with the type and concentration of dissolver used. It can be seen that K_2CO_3 was the most effective in dissolving the scale. What this plot does not show, however is the equilibrium concentration of total aqueous barium, which can affect the rate of conversion. This is shown in Figure 10, where the total aqueous barium is plotted against the addition of total carbonate. It can be seen that although the conversion with K_2CO_3 was complete, the aqueous concentration of barium was very small.

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Conclusions

A unique chemical simulation program has been developed which combines predictive models of an aqueous solution and a solid solution (co-precipitation) to represent the co-precipitation of Ra in barite. Such a tool can be effective in predicting the fate and processing of NORM and other related scales.

In any program however, to maximize the benefits from computer models, the range of their accuracy must first be obtained prior to calculation. This helps to increase the confidence of the calculated results.

Limitations to chemical simulations must be understood, both chemically and physically. This is extremely important when the conditions of the process to be simulated are not precisely known. For instance, efforts to predict scaling in production systems are limited because of unknown pressure and temperature effects of gas lift valves, submersible pumps, rod pumps and other production equipment. Consequently, scale prediction may be constrained because of limited knowledge of the physical system, rather than the chemical model.

If the accuracy range and external limitations are know in advance, then maximum utility can be obtained from this cost effective and time saving tool.

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Table 1. Standard State partial molal thermodynamic properties used in this study.

Species Name	Formula	ΔG°f cal/mole	S° cal/mole K	V° cm^3/mole	Cp° cal/mole K
barite	$BaSO_4$	-325,563[a]	31.6[b]	52.10[a]	33.80-3.43x10^5/T
	$RaSO_4$	-326,290[c]	33.0[b]	55.35[d]	19.06+0.01784*T
Ra^{2+}		-134,200[f]	13.0[f]	10.6[f]	-14.4[f]
Ba^{2+}		-134,030[f]	2.3[f]	12.60[f]	-12.3[f]
SO_4^{2-}		-177,930	4.5	72.04	-64.38

[a] Helgeson et al. (1978); [b] Wagman et al. (1982); [c] Sverjensky and Molling (1992); [d] Predicted from the correlation among barite isostructural family of solids, using the method of Zhang et al. (1990); [e] Estimated from the trend among alkaline earth sulfates Tolmach, (1995), [f] Shock and Helgeson (1988)

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Table 2. Simulation of the experimental data reported by Doerner and Hoskins (1925). Data extracted from Table IV of that reference. The first five experiments (IV-A-1 to 5) are rapid precipitation reactions with no agitation. The second four (IV-B-1 to 4) are slow precipitation reactions at elevated temperatures (not provided) and rapid agitation. The last three (IV-C-1-3) are precipitation by evaporation.

Experiment (Table IV-)	Ra (aq, final) (moles/l)x10^{-10}		Ba(aq, final) (moles/l)x10^{-4}		NORM Scale (ppt) (moles/l)x10^{-4}		Ra:Ba Solid Ratio (x10^{-6})		
	Obs.	Sim.	Obs.	Sim.	Obs.	Sim.	Obs.	Sim.	% Error
IV-A-1	1.54	1.28	19.1	19.2	8.67	8.67	0.081	0.114	33.7
IV-A-2	0.46	0.33	6.19	6.26	21.6	21.5	0.083	0.089	7.4
IV-A-3	7.39	5.94	9.76	9.83	8.45	8.46	0.883	1.05	17.6
IV-A-4	20.9	16.9	4.73	4.74	4.81	4.81	5.51	6.31	13.6
IV-A-5	47.8	42.7	2.15	2.15	2.08	2.09	33.7	36.2	7.2
IV-B-1	0.37		1.13	1.13	4.33	4.33	0.94	0.91	2.9
IV-B-2	0.30		1.01	1.02	4.45	4.45	0.93	0.90	3.1
IV-B-3	2.55		3.55	3.55	8.16	8.15	1.23	1.42	14.6
IV-B-4	0.83		1.53	1.53	1.20	1.20	1.15	1.12	2.7
IV-C-1	0.70	0.81	1.35	1.35	1.41	1.41	1.19	1.11	6.9
IV-C-2	0.51	0.55	3.88	3.92	1.58	1.58	0.28	0.26	8.0
IV-C-3	0.71	0.88	1.49	1.50	1.24	1.25	1.22	1.08	11.9

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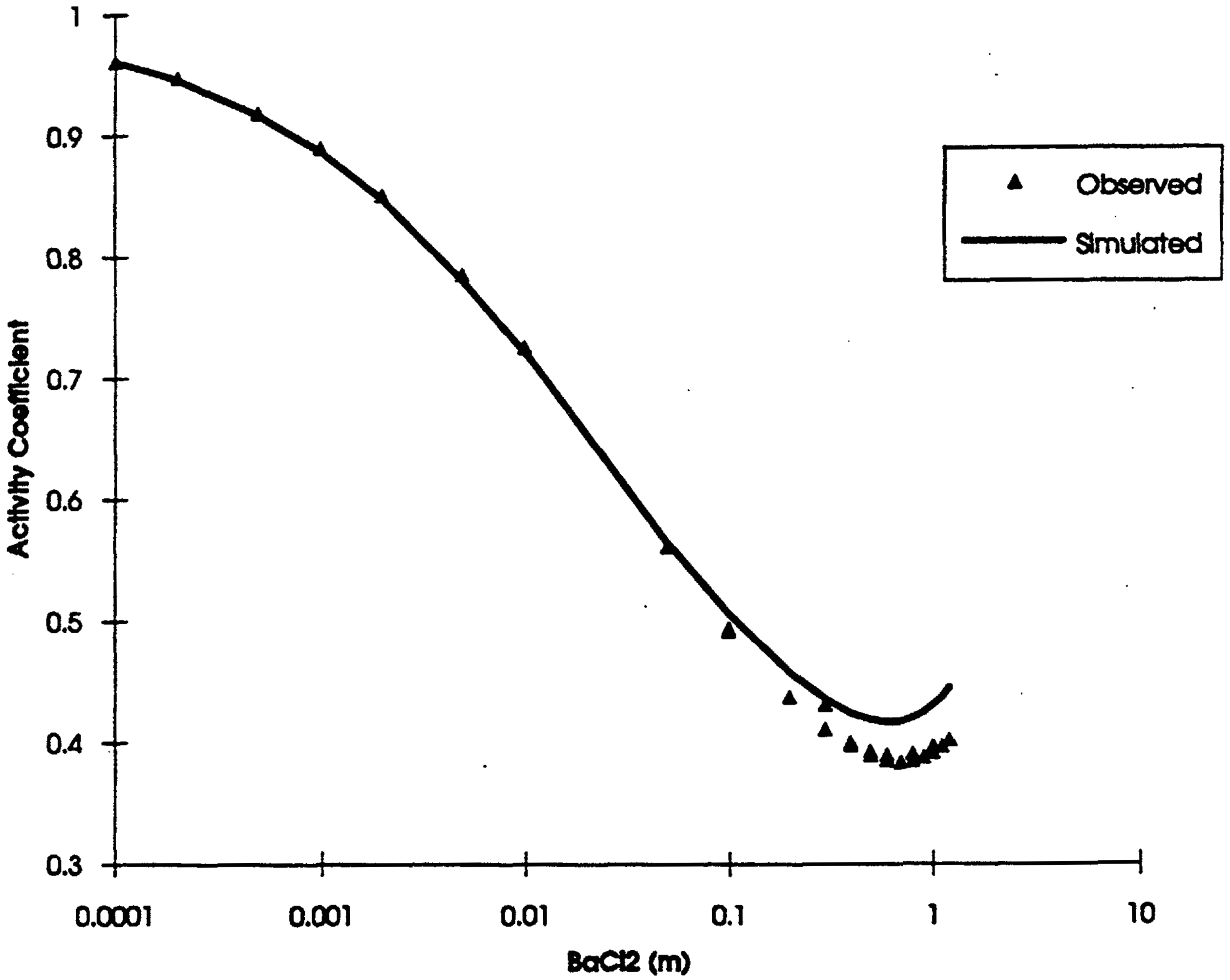

Figure 1. Plot of the simulated and reported mean activity coefficient for $BaCl_2$ at 25°. Experimental data was obtained from Lobo (1989), Tables 6c and 6g on pages 84 and 87. The points represent the reported data, the lines represent the simulation results.

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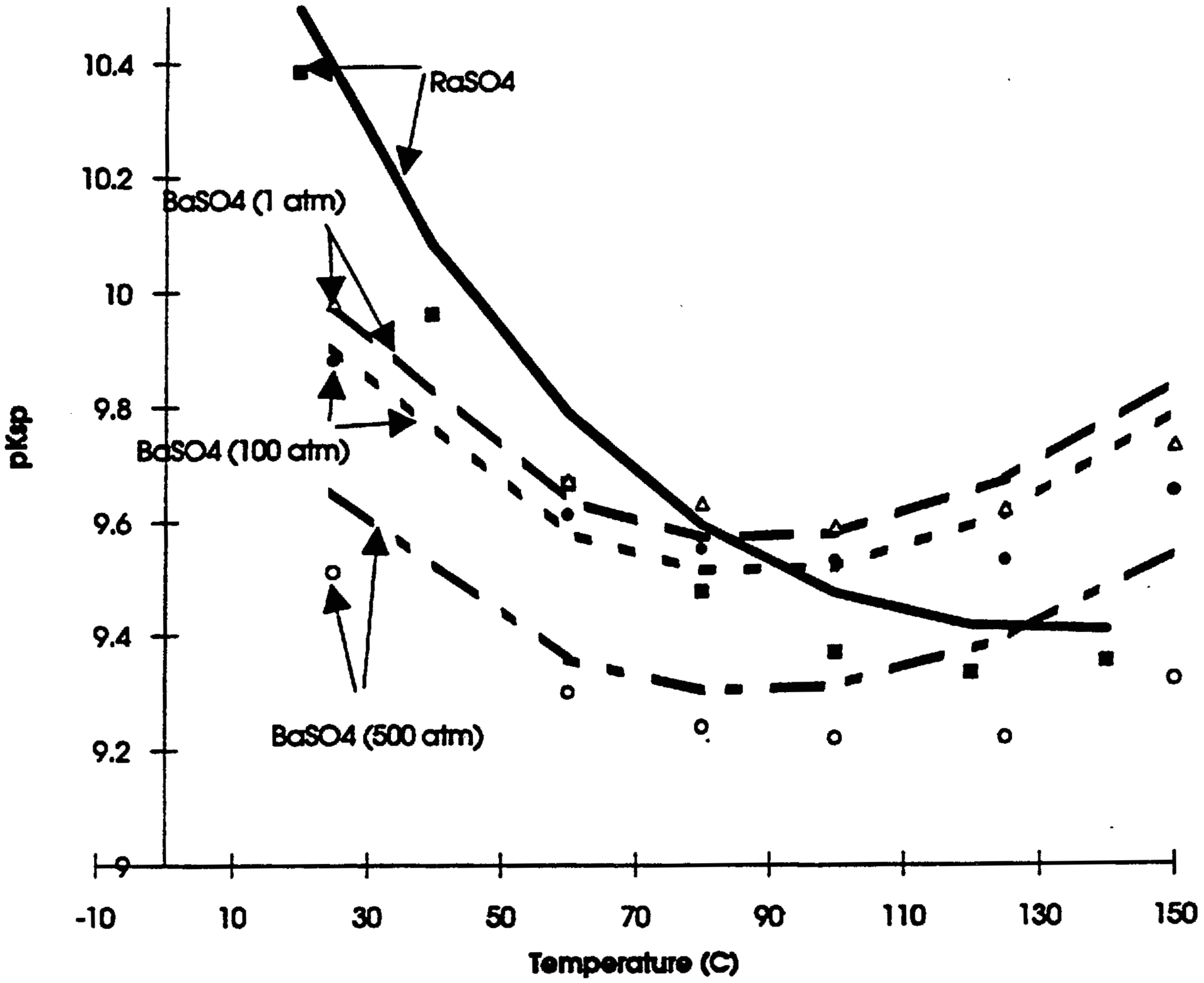

Figure 2. Plot of the simulated and reported temperature dependent solubility product constant (pKsp) for $RaSO_4$ and $BaSO_4$ between 20 and 150°C . The reported pKsp values for $RaSO_4$ were obtained using the equation provided by Langmuir and Riese (1985). pKsp values for $BaSO_4$ were obtained from Blount (1977). The points represent the reported data, the lines represent the simulation results.

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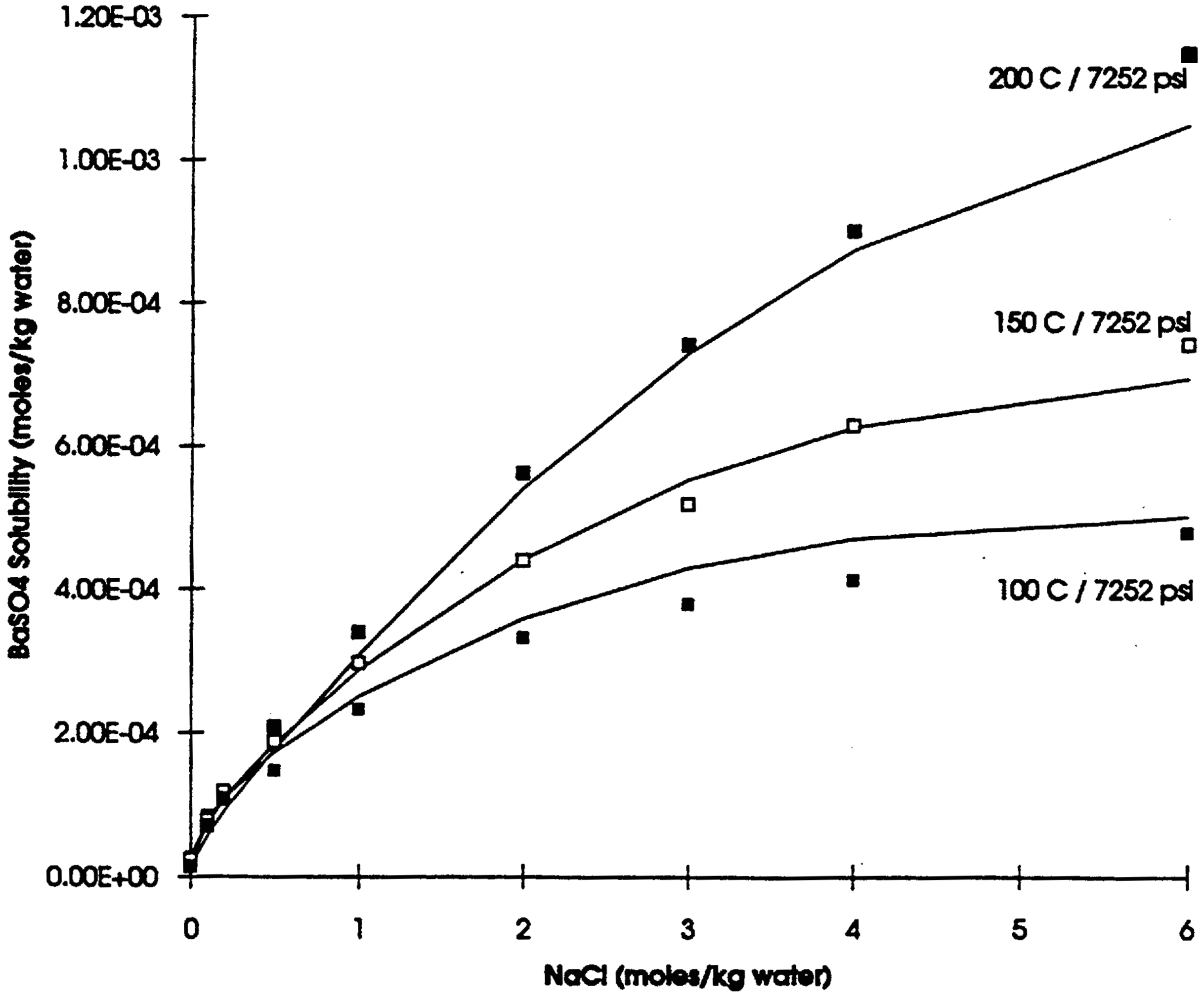

Figure 3. Plot of barite solubility as a function of NaCl concentration and temperature at 7262 PSI. Data was obtained from Blount (1978). The points represent the reported data, the lines represent the simulation results

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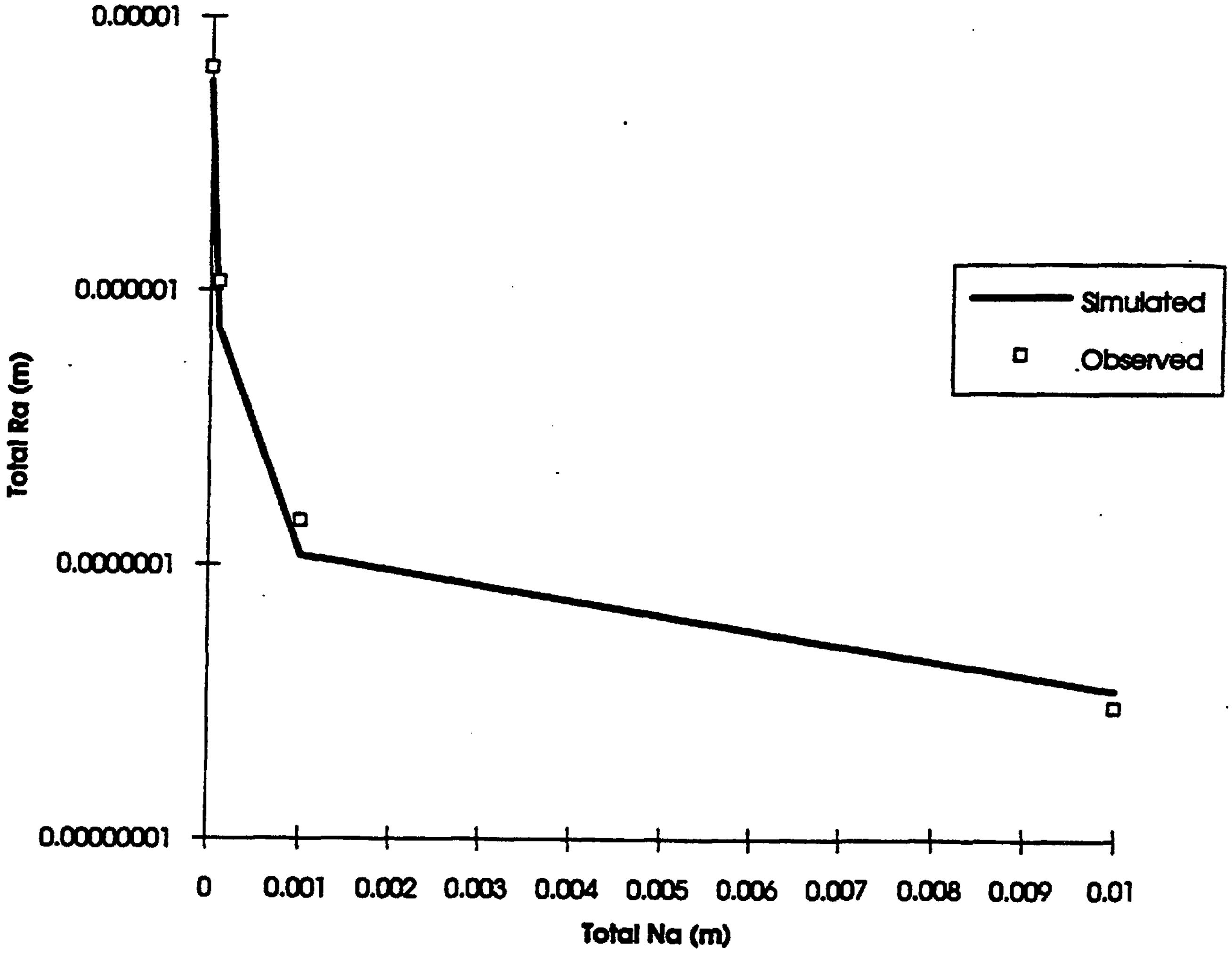

Figure 4. Plot of the simulated and reported solubility of $RaSO_4$ in water as a function of Na_2SO_4 addition. Experimental data were obtained by Nikitin and Tolmatscheff, 1933 (as reported by Langmuir and Riese, 1985) at 20°C and 0 molal ionic strength.

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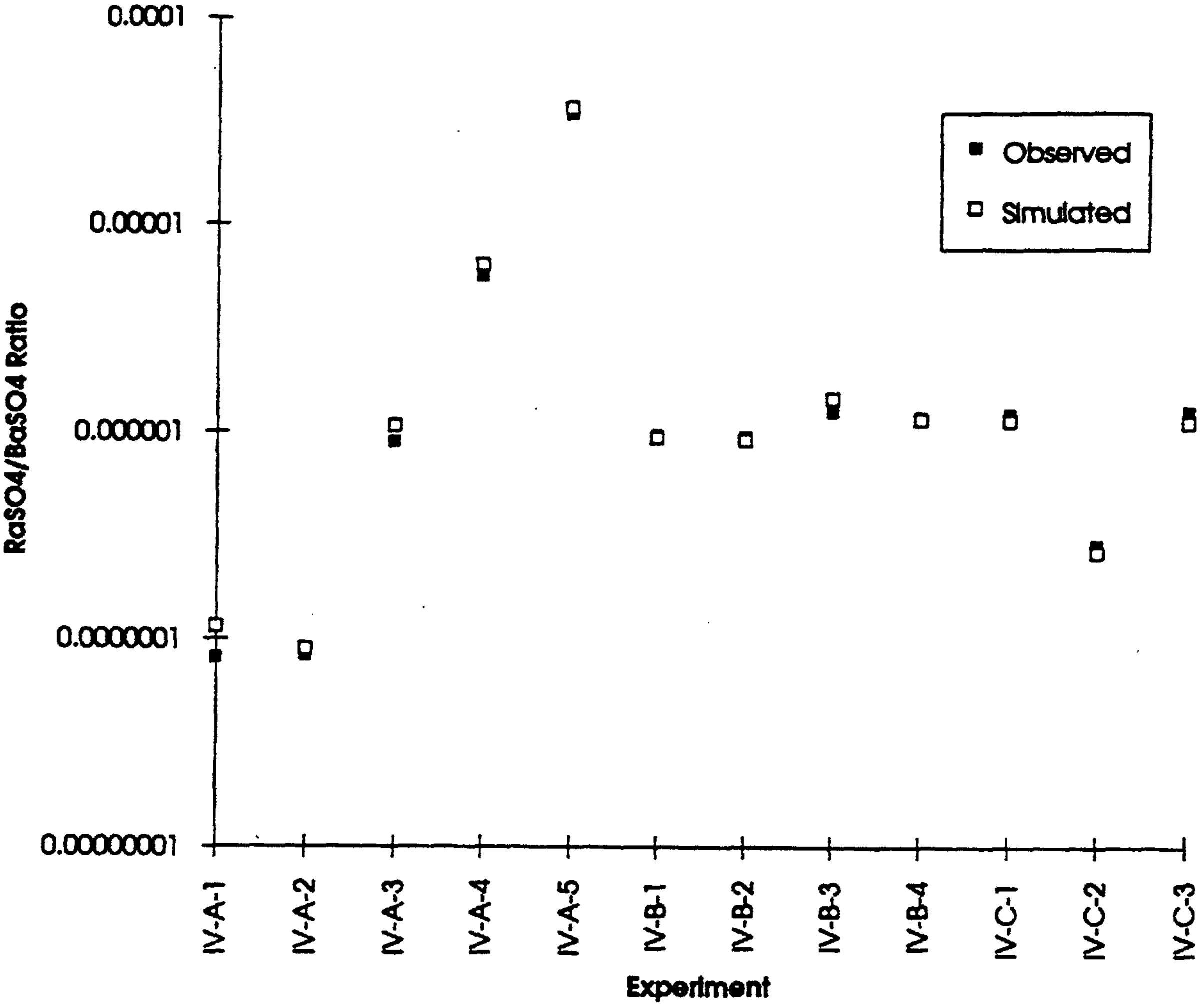

Figure 5. Plot of the observed and simulated Ra/Ba ratio in co-precipitated barite. These simulations are significant in that they determine the radioactivity of the solid. Data was obtained form Doerner and Hoskins (1925).

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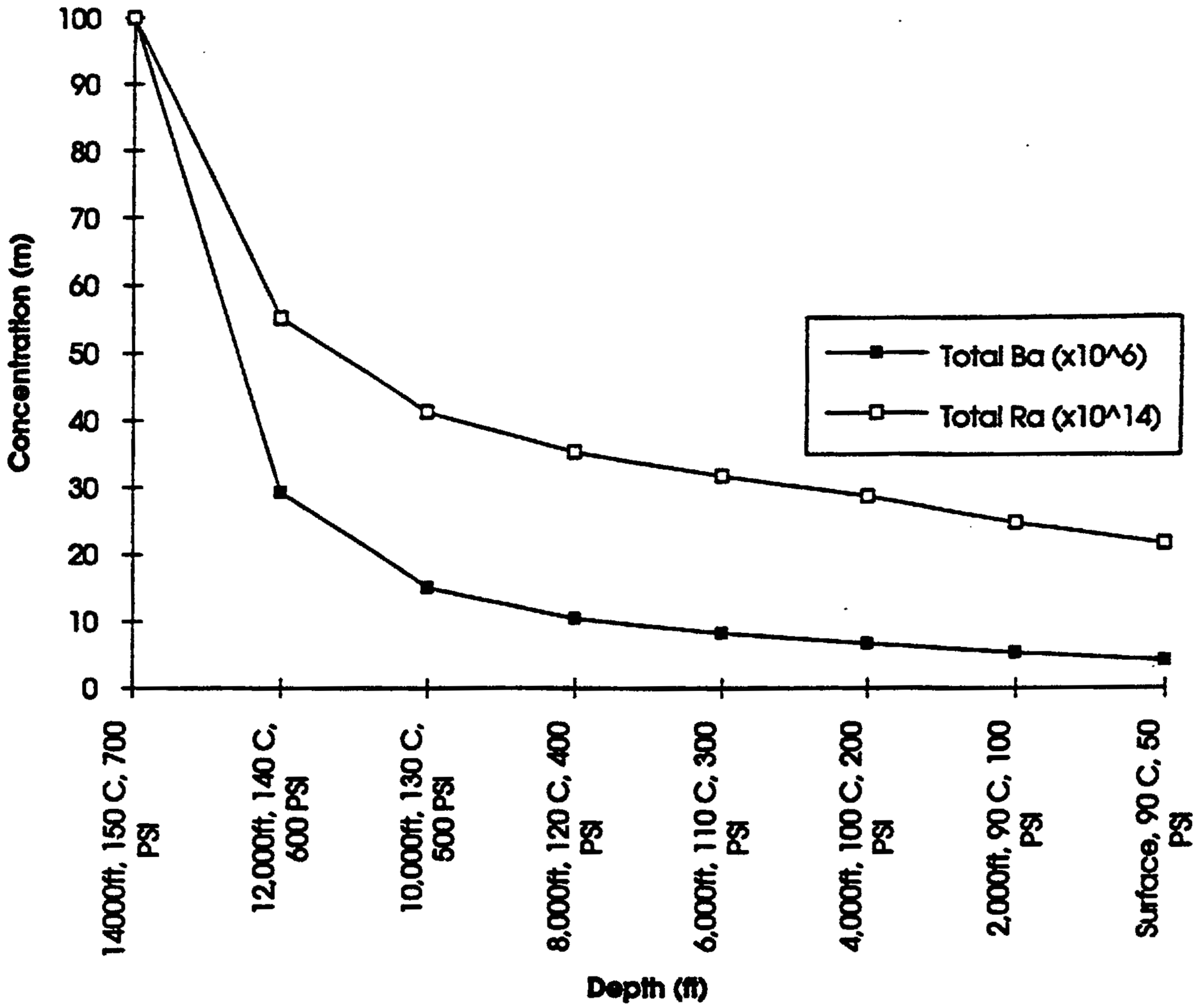

Figure 6. Simulation of NORM scaling in a production tubing. The total barium and radium concentration in the brine is plotted against depth, in order to simulate the decrease in concentration during brine production and NORM scaling. In this simulation, the well depth is 14,000 ft, the BHP is 700 atm, and the BHT is 150°C. Also, temperature and pressure are assumed to increase linearly with depth, and scaling is assumed to occur immediately when the system is supersaturated.

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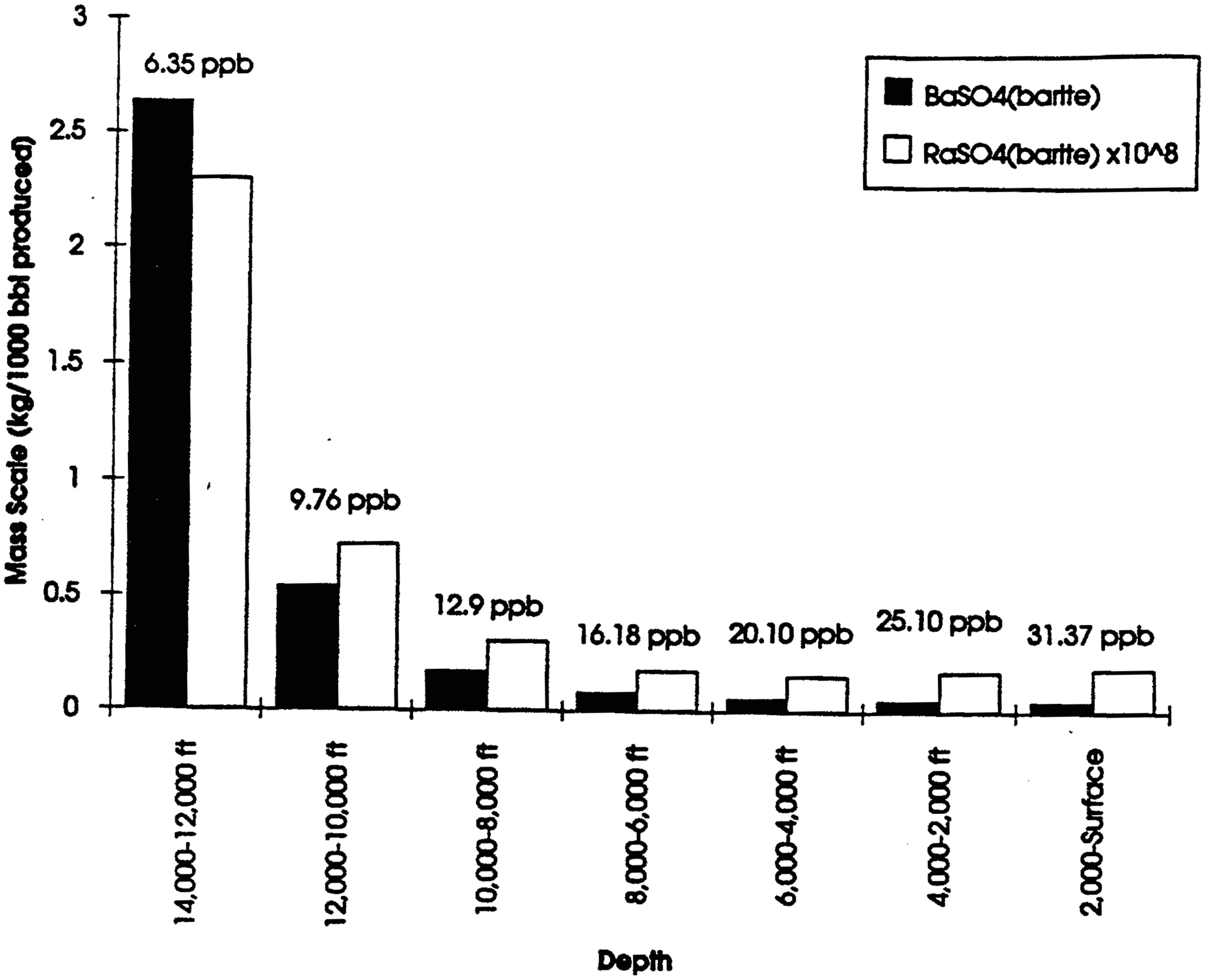

Figure 7. Simulation of NORM scaling in production tubing. Plot of the mass of NORM scale formed in the tubing as a function of depth. The mass of scale formed is based on 1000 bbl brine produced, and upon constant equilibrium in the brine (i.e. no supersaturation). In this simulation, significant of scaling occurred at 12,000 to 14,000 ft. The numbers above the columns represent the molar concentration of $RaSO_4$ in the $BaSO_4$ scale.

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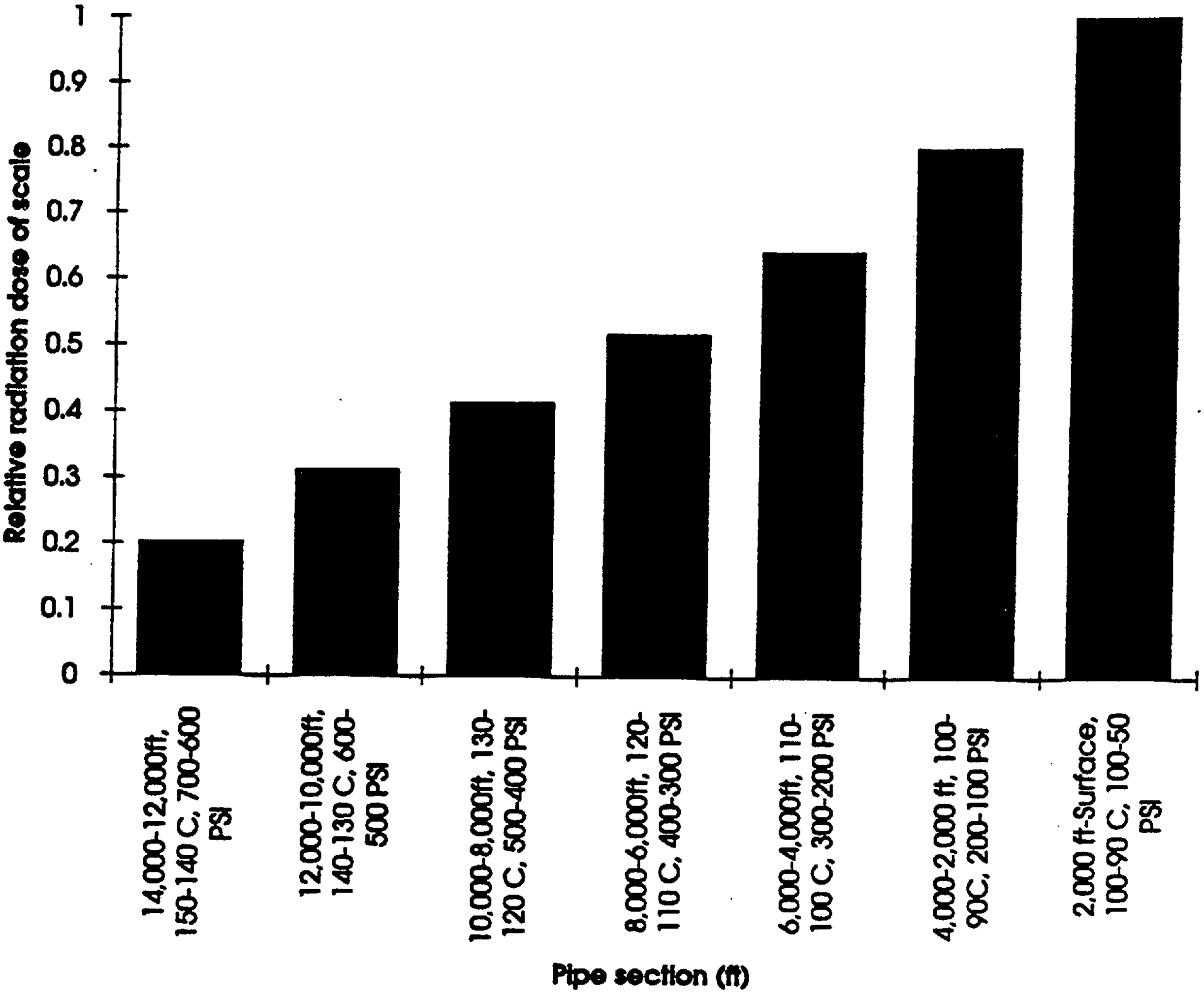

Figure 8. Simulation of NORM scaling in production tubing. Plot of the relative radioactivity of the scale formed in each section of pipe. The most radioactive scale was calculated to occur at the surface and was nearly five times more radioactive than the scale that formed at the bottom hole.

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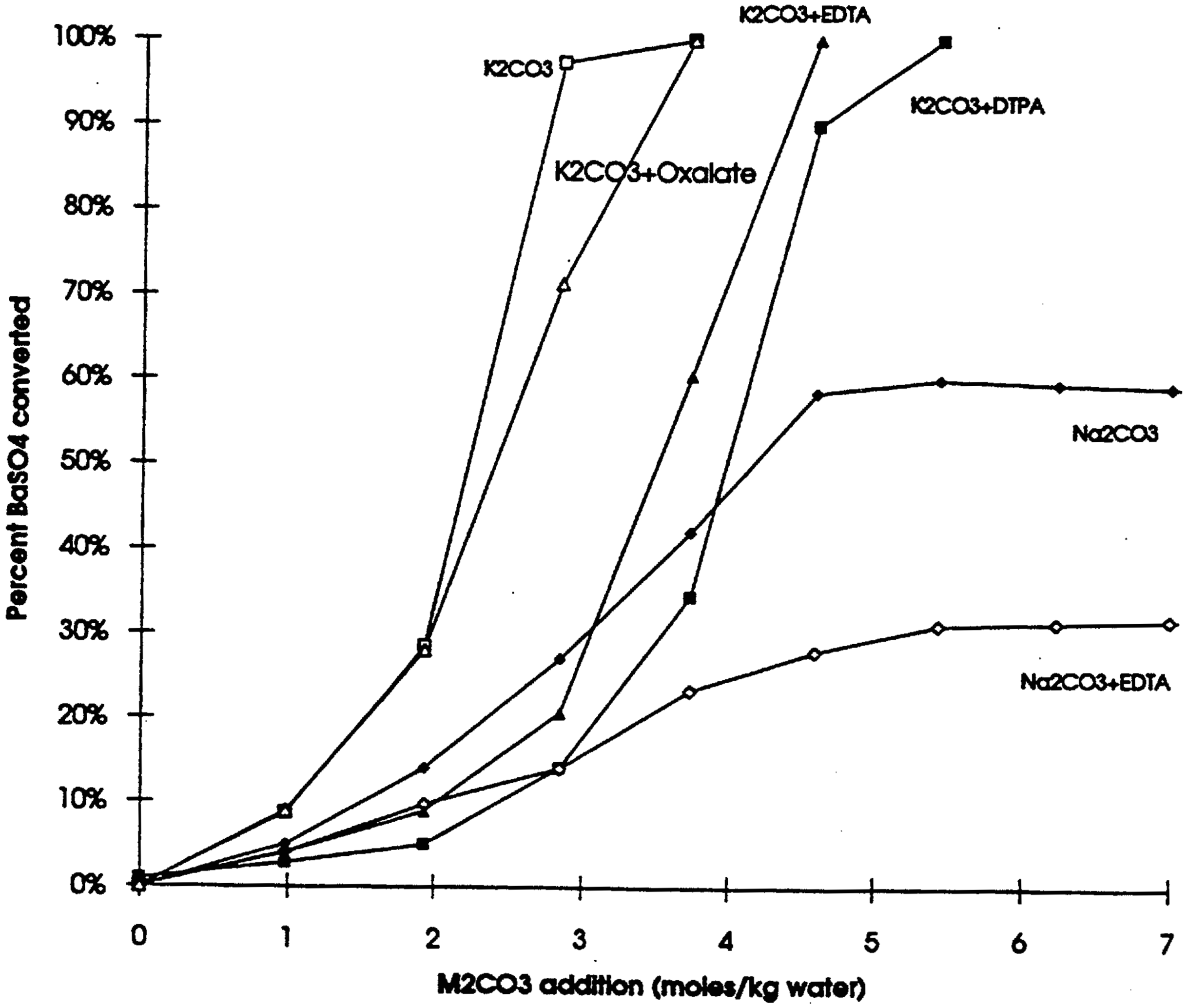

Figure 9. Plot of the percentage of NORM barite dissolved as a function of scale dissolver concentration. The effects of carbonate salt and chelating agent used are shown.

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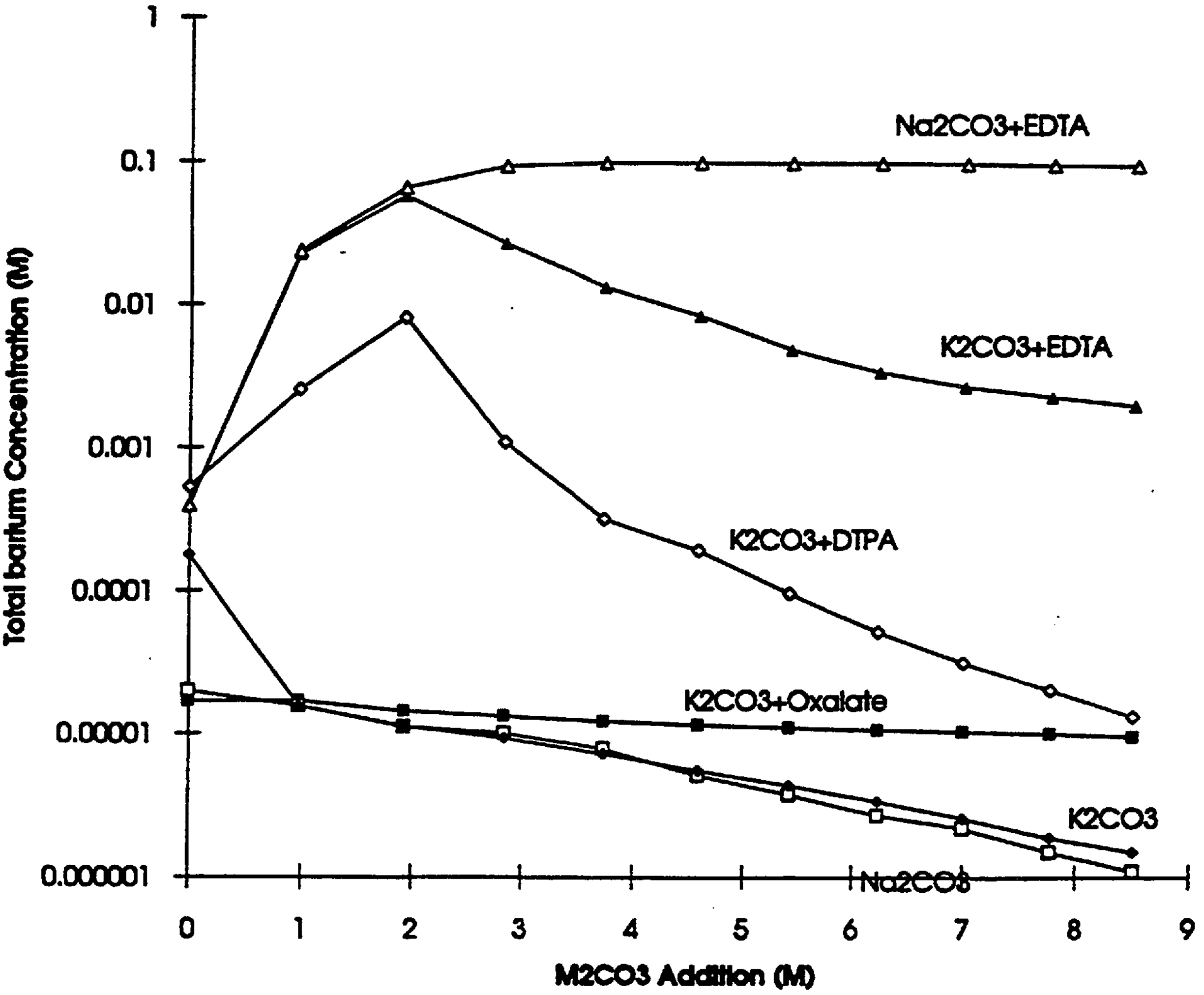

Figure 10. Aqueous concentration of barium as a function of scale dissolver concentration. The addition of chelant greatly increases the concentration of barium in solution.

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APPENDIX A

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APPENDIX B

CONFERENCE AGENDA

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PROGRAM

Naturally Occurring Radioactive Material Conference
October 17-18, 1995
Adam's Mark Hotel
Houston, Texas

October 16, 1995

Conference Registration	3:00 p.m. - 7:30 p.m.

October 17, 1995

Measurement and Survey Technical Session 8:30 a.m. - 11:45 a.m.

Dr. John Oddo, Water Research Institute, Inc.

Each presentation lasts approximately 25 minutes, with time for questions.

PAPER NO.	TITLE & AUTHOR
1	Determination of Naturally Occurring Radionuclides in Samples from the Oil and Gas Industry *Dr. G. Jonkers,* Shell - Amsterdam
2	Detecting NORM Contaminated Tubing During Pulling Operations *Mr. Thomas M. Williams,* Texaco Inc.
Break	9:45 a.m. - 10:00 a.m.
3	High Density Radiological Site Characterization Surveys for NORM Sites *Mr. C. R. Flynn,* Chemrad Tennessee Corp.
4	Methods for Estimating Dose to Individuals from NORM *Dr. J. L. Alvarez,* IT Corp.
5	Evaluation of Alternative Site Release Criteria *Mr. Alan McArthur,* Central Environmental, Inc.
6	Radioactive Lead: An Underestimated NORM Issue? *Dr. G. Jonkers,* Shell - Amsterdam

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Lunch 12:00 p.m. - 1:00 p.m.

Keynote Speaker: *Mr. George Walker*, Vice President of Health, Environmental & Safety, Unocal

Regulatory Issues and Activities Technical Session 1:15 p.m. - 2:30 p.m.
Chairman: *Mr. Kevin Grice*, Texaco

PAPER NO.	**TITLE & AUTHOR**
7	
8	Development of a Comprehensive NORM Program *Mr. Steve E. Woods*, Halliburton Energy Services
9	Potential Impact of Environmental Regulations on the Oil and Gas Exploration and Production Industry *Ms. Jeanette NewVille*, Chevron

Break 2:30 p.m. - 2:45 p.m.

PANEL DISCUSSION*

Regulatory Issues Panel 2:45 p.m. - 5:00 p.m.
Focus on Proposed and promulgated state and federal NORM regulations and their impact on the oil and gas industry.
*This discussion is designed for audience questions and participation.

Panel Moderator/Facilitator: *Mr. Kevin Grice*, Texaco

Panel Members:

Mr. Edgar D. Bailey, Chief, Radiologic Health Branch, California Department of Health Services

Mr. Mike Broderick, Environmental Program Administrator, Oklahoma Department of Environmental Quality, Radiation Management Section

Ms. Cindy Cardwell, Administrator, Standardization Branch, Texas Health Department

Mr. Wendall Carriker, Office of Hazardous Materials Technology, Research and Special Projects Administration, U.S. Department of Transportation, Washington, D.C.

Mr. Richard Lewis, Supervisor, Mississippi Oil and Gas Board

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Mr. Ray D. Paris, Chairman, Conference of Radiation Control Program Directors, Inc., NORM Commission; Manager, Radiation Control Section, State Health Division, Dept. of Human Resources, Portland, OR

Mr. Allan Richardson, Deputy Director, Office of Radiation and Indoor Air, U.S. Environmental Protection Agency

Ms. Leslie Savage, Assistant Director, Waste Management Environmental Services Section, Oil and Gas Division, Texas Railroad Commission

Mr. William Spell, Administrator, Radiation Protection Division, Louisiana Dept. of Environmental Quality

October 18, 1995

NORM Management and Disposal Technical Session **8:00 a.m. - 9:30 a.m.**
Chairman: *Dr. Lew Cook*, Chevron
Each presentation lasts approximately 25 minutes with time for questions.

PAPER NO.	**TITLE & AUTHOR**
10	Effective Removal of NORM Scale in the Rycroft Field *Mr. William G. F. Ford*, Halliburton Energy Services
11	Technical Profile of the Envirocare of Utah NORM Disposal Operation *Mr. Kevin C. Fuller*, Envirocare of Utah, Inc.
12	NORM Disposal Cost Study *Mr. Alan McArthur*, Central Environmental, Inc.
13	Modeling and Dose Assessment of NORM Injection in a Layered Geologic System *Dr. G. P. Williams*, Argonne National Laboratory

Break **9:30 a.m. - 9:45 a.m.**

PANEL DISCUSSION*

Legal Issues Panel **9:45 a.m. - 11:45 a.m.**
To address legal concerns in dealing with NORM issues and potential liability.
***This discussion is designed for audience questions and participation.**

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Panel Moderator/Facilitator: *Mr. Ed Pickel,* Shell U.S.A.

Panel Members:

Mr. Thomas M. McNamara, Partner, Liskow & Lewis, P.C.

Mr. David L. Martindale, Partner, Gibbes, Graves, Mullins, Ferris, Hartman & Harlow

Ms. Susan K. Carter, Attorney, Kean, Millen, Hawthorne, D'Armond, McCowan & Jarman

Mr. Richard Pabst, Texaco Legal Dept., Texaco E&P, Inc.

Lunch 12:00 p.m. - 1:00 p.m.

NORM Scale Prediction and Control Technical Session 1:15 p.m. - 5:00 p.m.
Chairman: *Dr. Mason Tomson,* Rice University

PAPER NO.	TITLE & AUTHOR
14	Controlling Barium Sulfate Scale Deposition by Inhibitor Squeeze in a Southern Texas Gas Well *Mr. Michael J. McKinzie,* Texaco, Inc.
15	A Laboratory and Field Study of the Mitigation of NORM Scale in the Gulf Coast Region of the United States *Dr. John Oddo,* WRI
16	Diagnosis and Prevention of NORM at Eugene Island 341-A *Dr. P. J. Shuler,* Chevron, U.S.A.

Break 2:30 p.m. - 2:45 p.m.

PAPER NO.	TITLE & AUTHOR
17	A Comparison of NORM Scale Dissolvers *Mr. Darrell L. Gallup,* Unocal Corp.
18	Remediation of Normally Occurring Radioactive Material (NORM) *Mr. Jim Orum,* AMBAR Technical Laboratories
19	Computer Simulation of Scales with NORM *Dr. A. J. Gerbino,* OLI Systems, Inc.

Closing Remarks

Dr. Tomson

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