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FURTHER DEVELOPMENTS IN THE IN-SITU REMOVAL OF TENORM FROM E&P PRODUCTION FACILITIES

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Abstract

At the 1997 NORM I Symposium in Amsterdam, we reported the technical feasibility of the in-situ removal of NOR-enriched scales (i.e. Technologically Enhanced NORM or TENORM) using scale dissolvers[1]. Subsequent investigations aimed at further development of the technology have highlighted process conditions under which decontamination to below current legislative threshold levels can not (yet) be achieved. Furthermore, in establishing residual surface contamination levels relative to legislative threshold levels, the F-factor as prescribed in the ISO 7503-1 procedure for wipe testing was found to be far too conservative. These and other findings are presented in this paper. In addition, their impact on contamination assessment methodologies and on the establishment of exemption/clearance levels applicable to the work practice of in-situ TENORM removal is discussed.

Background

A waterbath heater from a gas production facility in north-east The Netherlands has been used as test equipment in laboratory trials aimed at the in-situ removal of TENORM. This was done by firstly circulating an aqueous solution of a commercially available scale dissolver (CASD) through the unit using a protocol provided by the supplier. Such scale dissolvers, which are widely used within E&P operations when the formation of calcium, barium and strontium sulphate scales impairs oil and gas production, are commonly based on chelating chemistry and reportedly successfully applied in the dissolution of LSA scales. In the present case, application resulted in the rapid and complete removal of ^{226}Ra and progeny containing sulphate scales as well as ^{210}Pb containing sulphide and hydrocerrusite scales from the heater internals (note the different types of scales encountered). However, approximately 40% of the initial ^{210}Pb activity concentration remained in the waterbath heater, leaving a calculated surface contamination of up to 20 Bq[^{210}Pb]/cm^2 that could not be removed by wipe testing. This level of contamination exceeded the level currently applied by Dutch authorities in the transport decree for the "classification" of contaminated material, namely 4 Bq/cm^2 β-/γ-emitting nuclides and 0.4 Bq/cm^2 for α-emitting nuclides (wipeable contamination).

Subsequent investigations established that the remaining surface activity could be attributed to metallic lead containing ^{210}Pb as either a surface deposit (originally underlying the scales) or intermetallically bound within the carbon steel matrix of the heater internals. The deposit can possibly be explained by the occurrence of the electrochemical (surface) reaction:

$$Pb^{2+} + Fe^0 \rightarrow Pb^0 + Fe^{2+}$$

produced water serving as the carrier phase for the lead ion. A further investigation was instigated to establish whether the lead deposit could be dissolved using 15% v/v acetic acid to which had been added 1% v/v of a strong oxidant such as potassium permanganate[2]. Circulation of this solvent resulted in the lowering of the residual ^{210}Pb surface contamination from the initial 20 Bq/cm^2 to 6 Bq/cm^2.
Internal inspection of accessible parts of the waterbath heater after this treatment revealed the presence of a thin layer of manganese dioxide precipitate, which was found to contain the ^{210}Pb responsible for the residual and wipeable surface contamination. To investigate whether this could be removed, a 0.5 molar citric acid solution was circulated through the waterbath heater. Following this treatment, wipe tests showed a remaining surface contamination of 0.2 Bq/cm^2.

Full decontamination to below threshold levels for wipeable radiological surface contamination was thus demonstrated. However, the requirement for three successive solvent treatments, each with water spacer flushes, was seen to be too cumbersome for field application. Further investigations were therefore instigated to attempt optimisation.

Optimisation Studies

In dissolution studies of pure lead foil had been established that acetic acid plus hydrogen peroxide could be used to dissolve metallic lead without the adverse generation of secondary precipitates. A TENORM-contaminated (two types of scales with overall activities of 2000 Bq [^{226}Ra]/g and 600 Bq [^{210}Pb]/g) section of the waterbath heater inlet line was used to ascertain whether this solution could be applied without causing excessive corrosion of the carbon steel. A similar approach was used as in the previous study. The CASD solution remaining from the experiments with the waterbath heater was first circulated through the line, and this was followed by circulating with a 15% v/v acetic acid plus 1% v/v hydrogen peroxide solution following a water flush. Contrary to the experiences gained with the waterbath heater, results (Table 1) showed the incomplete removal of sulphate scale (inclusive ^{226}Ra and its progeny in these scales), residual presence of both metallic lead and lead-containing sulphide and hydrocerrusite scales (containing ^{210}Pb) and the formation of a radiologically contaminated iron oxide deposit. After cutting the tube into three pieces, to allow adequate sampling and measurements, it was estimated that a removable surface contamination (using standard wipe testing) of 0.15 Bq [^{226}Ra]/cm^2 and 0.08 Bq [^{210}Pb]/cm^2 was present. However, γ-spectrometry demonstrated that also a non-removable contamination of 3.1 Bq [^{226}Ra]/cm^2 and 1.0 Bq [^{210}Pb]/cm^2 remained.

Several possibilities were envisaged as to why the treatment remained unsuccessful when judged against current legislative threshold levels. The chelating capacity of the CASD solution may have been sub-optimal or the morphology and/or density of the scales in the inlet line may have been different to that of the scale in the waterbath heater. Subsequent investigations showed that all of these possibilities could be discounted. Therefore, in the absence of an obvious explanation, it was decided to repeat the experiments using various sections of TENORM contaminated flow-lines newly dismantled from the surface facilities of the previously mentioned gas production facility.

The TENORM contamination of three flowline sections of 0.9 – 1.5 metre lengths was mapped by means of an internal sampling and analysis programme (Table 2). Each section was then subjected to a decontamination treatment that differed only in the type of CASD solution and lead solvent used (Table 3). The TENORM contamination remaining after the treatment was characterised and quantified through γ-spectrometric analysis (Table 4). From the results is evident that > 99% removal of the TENORM contamination has been achieved, the decontamination treatment applied to flowline section B giving the overall best result. The remaining activity was found to be concentrated in so-called pits, i.e. relatively shallow holes in the metal wall of the flowline sections resulting from extremely localised corrosion that had occurred in the time that the gas production facility was in operation. Barium was encountered in these pits. This suggests that scale had accumulated in the pits, the very nature of the pits contributing to an inaccessibility of CASD solutions and lead solvents during the decontamination trials. The area around the pits was observed to be clean and wipe testing was now required to confirm whether the residual surface contamination of this area was below threshold levels.

Evaluation of Surface Contamination

In wipe testing, a defined area (usually 100 cm^2) is wiped off with an ethanol-wetted tissue. This tissue is analysed for either total α-activity and total β-activity, or it is analysed for specific radionuclides such as ^{226}Ra and ^{210}Pb. This latter method yields the surface activity concentrations, from which the total α-activity and β-activity (in Bq/cm^2) is (conservatively)[3] calculated via:

$$\text{Total } \alpha\text{-activity} = 4*[^{226}\text{Ra}] + 1*[^{210}\text{Pb}] + 1*[^{228}\text{Ra}] + 4*[^{224}\text{Ra}]$$

$$\text{Total } \beta\text{-activity} = 2*[^{226}\text{Ra}] + 2*[^{210}\text{Pb}] + 2*[^{228}\text{Ra}] + 3*[^{224}\text{Ra}]$$

In order to determine the total removable activity on any surface by means of wipe testing, the norm ISO 7503-1 prescribes that the measured activity on the wipe test tissue should be multiplied by the reciproke of the efficiency factor F, where:

F = Ap (i.e. the removed activity)/A_t (i.e. the total removable activity)

When no experimental values are available, a conservative value of F = 0.1 must be used. On-line spectroscopy (if properly calibrated) provides the total removable and non-removable surface activity concentrations; in this case no F factor needs to be taken into account.

In applying the standard as prescribed, a total alpha surface contamination below the threshold level of 0.4 Bq/cm^2 was not achieved in any of the decontamination treatments described above (Table 5). However, in our experiments we have found the F-factor as prescribed in ISO 7503-1 to be far too conservative.

Determination of F factors

Because of the influence of F on the determination of the total activity remaining after decontamination, it was determined experimentally. To this end, two pieces of flowline section B were wiped 10 times in succession and once again after 6 and 12 days. Results from these wipe tests are shown in Figure 1 (first piece) and Figure 2 (second piece). Based on these results, a value of F = 0.4 ± 0.1 has been established for both ^{226}Ra and ^{210}Pb. Applying this F factor to the results, it is seen (Tables 4 and 5) that although the treatment of flowline section B gave the best decontamination result in terms of Bq/g, decontamination to below the threshold level for wipeable contamination was not achieved. It is remarkable that for both pieces a gradual decrease in the removed surface activity is observed in the first ten wipe test but that after 6 and 12 days the amount of removable surface activity increases again. The mechanism by which ^{226}Ra and ^{210}Pb are again liberated is unknown, although it was established after the decontamination treatments a non-removable activity of 1.46 Bq[^{226}Ra]/cm^2 and 0.98 Bq[^{210}Pb]/cm^2 had remained in the flowline sections. It seems obvious that this must be the source of the renewed ingrowth of removable surface activity. A similar sort of ingrowth was noted in the waterbath heater when carrying out wipe tests one year after decontamination.

Further Investigations

From the optimisation studies described above was concluded that the marginal improvement required to achieve decontamination to below threshold wipeable surface contamination levels could possibly be realised by extending the duration of the treatment. Consideration was also given to increasing the rate of circulation to improve pit accessibility. However, since the removal of scale from pits would not be transport limited (i.e. hydrodynamics does not play a significant role in system performance), this consideration was discarded. The extended duration treatment was performed on a bent pipeline section taken from the separator inlet of the gas production facility. The treatment was analogous to that described in Table 3 under Section B, albeit that the CASD solution was circulated for a period of 168 hours at an application temperature of 70°C. Use was made of the acetic acid/hydrogen peroxide lead solvent, since this appeared to be the most successful from previous experiments. The solvent was circulated for 24 hours at an application temperature of 50°C. From the results (Table 6) can be concluded that extending the duration of the treatment did not yield the desired result.

During and after circulation of the lead solvent, the ^{210}Pb activity in the solvent was observed to decrease, indicating that the lead was precipitating from the solution. After the treatment a grey LSA precipitate was noted on the inside surface of the vessel containing the lead solvent as well as on the surface of the heating coil, explaining the increase in residual ^{210}Pb surface contamination. The precipitate, which consisted mainly of galena (PbS) and goethite (FeOOH), contained activity concentrations of 290 Bq[^{226}Ra]/g and 600 Bq[^{210}Pb]/g. The mechanism by which this deposit was formed is unknown. In the pipeline section itself some rust had accumulated containing activity concentrations of 61 Bq[^{226}Ra]/g and 30 Bq[^{210}Pb]/g.

Discussion

The tests described in this paper indicate that chemical dissolution techniques can remove 95% - 99% of the TENORM activity concentrations. However, even when taking into account a realistic wipe efficiency factor, this result is not satisfactory to meet the current stringent demands for the unrestricted re-use of in-situ decontaminated equipment.

The deposition of TENORM in E&P production facilities is very inhomogeneous, both in radionuclide distribution as in the total mass of deposited material and in composition of deposits. Also, there is a significant difference in deposition at the top and at the bottom of flowlines. These large differences in local 'environment of deposition' may contribute to not achieving full decontamination.

During in-situ decontamination (in particular during lead dissolver treatments which are carried out at elevated temperatures and where the presence of oxygen cannot be avoided) deposits are generated, presumably originating from corrosion. Radionuclides liberated from contaminated surfaces apparently can be strongly absorbed on or even incorporated in these deposits. This also contributes to not achieving full decontamination.

Yet another contributing factor has been observed from scanning electron microscopy pictures of decontaminated surfaces. Barium and lead compounds (with their associated ^{226}Ra and ^{210}Pb radionuclides) remain in pits and (iron) oxide matrices on the inner surfaces of flowlines and equipment. It is likely that these pits are inaccessible to the chemical dissolvers. Also, the oxide matrices are not easily removed with chelating agents and the weak organic acids of the lead dissolver solution.

A large volume of (liquid) waste has resulted from the decontamination experiments. Approximately 1200 kg of CASD with an average activity concentration of 3-4 Bq[^{226}Ra)/g and 1-2 Bq[^{210}Pb]/g, and about 300 kg of lead dissolver and rinse water with an average activity concentration of 1-2 Bq[^{210}Pb]/g remain. A major restriction for the application of in-situ decontamination is the costs for the disposal of this 'radioactive' liquid waste. If alternative disposal techniques (i.e. re-injection into suitable sub-surface formations such as depleted oil/gas reservoirs[1]) can not be agreed upon with the competent authorities, volume reduction of the generated liquids remains the only option for cost reduction. However, currently no technically and/or economically attractive techniques for volume reduction of these liquid waste streams have been developed.

Conclusions

The application of a combination of a chemical scale dissolver with a lead specific solvent can remove 95% - 99% of TENORM activity present in E&P production facilities. This degree of decontamination is not sufficient to meet current regulatory demands in The Netherlands.
Due to chemical interactions of the lead dissolver with the iron matrix, precipitates may be formed which are not easily removed and which also adsorb/incorporate some liberated radionuclides. Further research is being carried out to develop protocols which prevent the occurrence of these interactions.
For the wipe efficiency factor F (ISO 7503-1), the prescribed value of 0.1 is very conservative. Work described in this paper indicates a value of 0.4 (0.1 to be more appropriate.
The re-appearance of ^{210}Pb on initially decontaminated surfaces significantly limits the realisation of compliance with maximum allowable surface contamination limits for the unrestricted re-use of equipment (parts).
The current state of the art of chemical in-situ decontamination leads to the production of significant volumes of (liquid) 'radioactive' waste, for which currently the only permissible but economically very unattractive disposal route in The Netherlands is via COVRA. This assumes the availability of this disposal route, which, on basis of information currently available to the authors, is unlikely.

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TABLE 1: SUMMARY DECONTAMINATION INLET LINE WATERBATH HEATER

	^{226}Ra (kBq)	^{210}Pb (kBq)
Initial total activity	549	193
Removed with CASD flush	390	160
Removed with acetic acid/hydrogen peroxide flush	130	23
Removable surface contamination	1.4	0.7
Percent removal achieved	95	95

TABLE 2: RADIONUCLIDE CONTAMINATION IN FLOWLINE SECTIONS

Location	^{226}Ra (Bq/g)	^{210}Pb (Bq/g)
"loose" deposits top	300 – 400	100 – 150
"loose" deposits bottom	250 – 400	70 – 100
"scrapings" top	125 – 135	30 – 40
"scrapings" bottom	1200 – 2000	300 – 600

Scale characterisation (XRD analysis)	$Ba_{(1-x)}Sr_{(x)}SO_4$;FeOOH(goethite);Fe_3O_4(magnetite); $CaCO_3/FeCO_3$
Scale surface density (g/cm^2)	0.006 – 0.07 (average 0.036)

TABLE 3: DECONTAMINATION TREATMENTS FLOWLINE SECTIONS

Section A	Section B	Section C
☐ Flush with degreaser ☐ Flush with clean water ☐ Flush with CASD solution A (50% solution; 75°C; 6 hrs.) ☐ Flush with clean water ☐ Flush with 15% acetic acid/1% potassium permanganate solution (50°C; 6 hrs.) ☐ Flush with 10% citric acid (room temp.; 16 hrs.) ☐ Flush with clean water	☐ Flush with CASD solution B (50% solution; 75°C; 6 hrs.) ☐ Flush with clean water ☐ Flush with 15% acetic acid/1% hydrogen peroxide solution (50°C; 6 hrs.) ☐ Flush with clean water	☐ Flush with degreaser ☐ Flush with clean water ☐ Flush with CASD solution C (85-90°C; 6 hrs.) ☐ Flush with clean water ☐ Flush with commercially available lead solvent (10% solution; 85-90°C; 6 hrs.) ☐ Flush with clean water

TABLE 4: RESULTS OF DECONTAMINATION TREATMENTS FLOWLINE SECTIONS

	^{226}Ra (Bq/g)	^{210}Pb (Bq/g)	Observations
Section A	0.17 – 0.32	0.07 – 0.11	Citric acid adduct precipitate formation
Section B	0.10 – 0.17	Up to 0.03	Iron oxide precipitate formation
Section C	0.11 – 0.41	Up to 0.12	No precipitate formation

TABLE 5: AVERAGE RESIDUAL REMOVABLE SURFACE CONTAMINATION

			F = 0.1	F = 0.4
	^{226}Ra (Bq/cm^2)	^{210}Pb (Bq/cm^2)	Total α-activity	Total α-activity
Section A	0.031	0.016	1.40	0.35
Section B	0.046	0.014	1.98	0.50
Section C	1.3	0.3	55	14

TABLE 6: RESULTS EXTENDED DURATION DECONTAMINATION TRIAL

	Residual ^{226}Ra (Bq/cm^2)	Residual ^{210}Pb (Bq/cm^2)
Long end after bend	0.31	0.34
Short end after bend	0.56	2.32

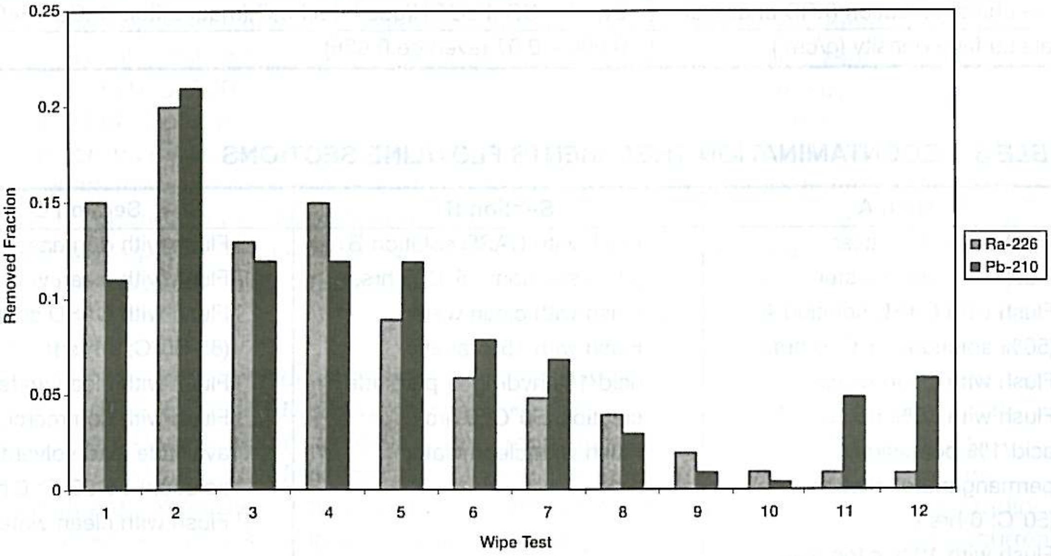

FIG. 1: WIPE TESTS FIRST PIECE FLOWLINE SECTION
Fraction of Ra-226 and Pb-210 removed in sequential wipe tests

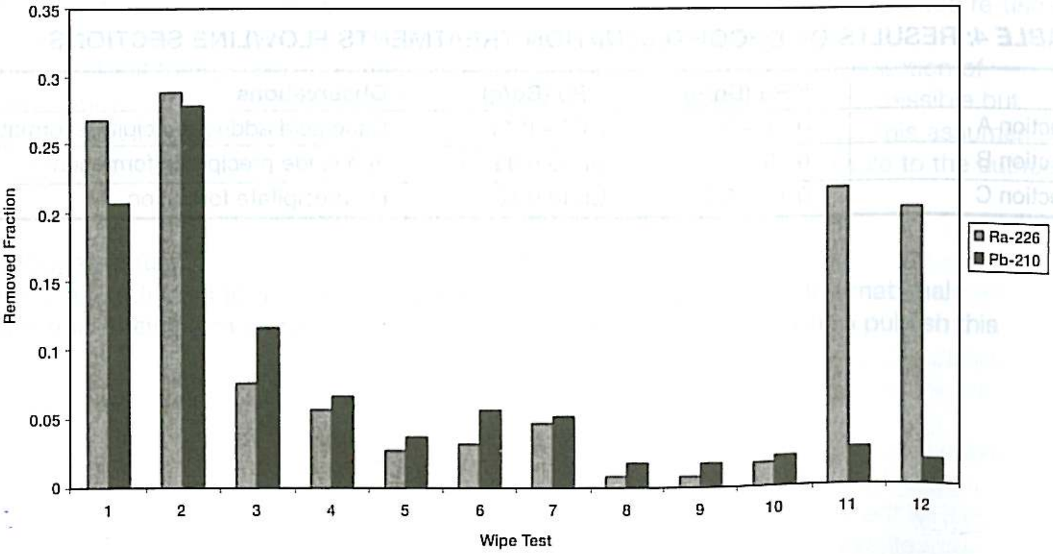

FIG. 2: WIPE TESTS SECOND PIECE FLOWLINE SECTION
Fraction of Ra-226 and Pb-210 removed in sequential wipe tests

References

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