Advanced methods for re-use and disposal of TENORM

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ABSTRACT : In general, TENORM is the acronym for **T**echnologically **E**nhanced **N**aturally **O**ccurring **R**adioactive **M**aterial. The elevated radionuclide concentrations are the result of chemical or physical processes taking place during exploitation or (re-)processing of raw materials.
While implementing EURATOM guideline 96/29 in the German legislation, in June of 2001 an essential pre-condition was created for re-use or disposal of TENORM. An essential progress has been achieved allowing to re-use TENORM or to dump it together with other residuals and waste, if the specific activity do not exceed the limits defined in the Radiation Protection Ordinance (StrlSchV). Otherwise, if the specified limits in terms of concentration or radiation dose are exceeded, than these materials must remain under radiological protection.
A practical application of the new German regulation turns out to be difficult especially for highly contaminated residuals taking into account problems arising from adaptation of the respective legislation on radiation protection, soil protection, waste management and transportation of dangerous goods.
The report tackles new chances of re-use and disposal of some TENORM arising from the new legislation taking into account different levels of contamination. Some options for re-use and disposal of selected TENORM will be described and evaluated. The problems arising from the licensing procedure will be discussed and elucidated how significant obstacles of the foreseen disposal ways can be overcome.

1 INTRODUCTION

The acronym TENORM summarizes solid substances which are resulting from physical or chemical processes applied in exploitation or processing of mineral raw materials or reprocessing of mineral by-products and wastes. In many cases the radionuclides of the natural decay chains ar not in radioactive equilibrium due to its different physical-chemical properties. Furthermore, TENORM often contain heavy metals and sometimes organic compounds. Their radioactivity may cause an enhanced exposure to both, workers and members of the public.
The defined concentration level for “enhanced” is derived from the annual dose limit for members of the public considering basic exposure scenarios. In Germany and some other EU member states this dose limit is 1 mSv/yr from which a minimum specific activity of 0.2 Bq/g per radionuclide of the U 238 decay chain and the Th 232 decay chain was derived. Subsequently, natural or processed materials with lower specific activities turn out from radiation protection regulation.
In preparation of the new German Radiation Protection Ordinance (StrlSchV) it was decided to include a list of such materials with enhanced natural radioactivity (s. Annex XII, part A of

StrlSchV) which can be realy expected in Germany. That was the outcome of investigations carried out during the drafting of this regulation. This list comprises sludge and scales from the exploitation of natural gas and crude oil and residues and by-products from processing of raw phosphate, iron and non-iron ores and minerals. In contrast to Germany, the most EU member states defined for their national radiation protection regulations only a minimum level of the specific radioactivity independently of the kind and origin of the material.
According to actual investigations [1] in Germany the precipitates (scales) in tubes from the extraction of natural gas and crude oil seem to be of prior importance due to high enrichment of radium isotopes and its decay products and the presence of metallic mercury. Therefore the following explanations are focused to different options of the re-use and disposal of such materials.
In addition, the problems connected with the re-use of slag from former copper smelting will be discussed.

2 RECENT SITUATION

The report [1] contains an overview on the kind, amount and range of specific activities of TENORM in Germany includung such TENORM which are not listed in the German Radiation Protection Ordinance, e.g. scales from geothermal applications and sludge from water treatment. The following explanations are only directed towards scales and sludge from oil and gas extraction and slag from copper melting.

2.1 Oil and gas extraction

Naturally occurring radionuclides are present in varying concentrations througout hydrocarbon reservoirs. The type of rock formation largely determines the radionuclide content of the reservoir; sedimentary rocks show low radionuclide concentrations whereas phosphate rock types have high levels. The waters associated with the rock formations often contain barium, calcium strontium and radium. During the oil and gas extraction barium precipitates as sulfate inside the tube. Radium isotpes are co-precipitating due to their chemical similarity to barium. Consequently, the radioactivity of the scales result primarely from Ra 226 and Ra 228. The long-living daughter products, i.e. Pb 210 and Po 210 and Th 228 regrow in relation to its physical half life compared to the half life of Ra 226 and Ra 228, respectively. Therefore the specific activities of Pb 210 and Po 210 will grow up to that of Ra 226, whereas the specific activity of Th 228 will exceed the Ra 228 activity by a factor of 1.46 (flow equilibrium). Sometimes Pb 210 is enriched against Ra 226 if the connate waters contain high amounts of lead.
According to [2] the specific activities of Ra 226 and Ra 228 in scales from the German oil fields may reach 300 Bq/g and 390 Bq/g, respectively. The maximum concentrations of these radionuclides from gas fields amount up to 650 Bq/g and 360 Bq/g, respectively [3]. Nevertheless, Ra 226 concentrations above 50 Bq/g were measured only at about 5% of the analysed scales from the gas fields in Saxony-Anhalt [4].
Based on a roughly calculation in [5] the annual amount of scrap from all German on-shore oil and gas extraction units is about 10.000 t containing approximately 1.000 t scales. The rise of sludge containing more than 100 Bq/g cross activity is given in [1] with 400 m^3/yr per off-shore oil extraction unit and 50 m^3/yr per on-shore extraction unit. The amounts of contaminated sludge from natural gas extraction are ten times lower.

2.2 Copper slate smelting

Copper slate mining and smelting in Germany was finnished in 1990. Beside the huge amount of waste rock material from the former copper slate mining, a lot of smelting residues such as copper slag and Theissen mud is still remaining in the landscape. According to [1] about 3 Million m^3 of copper slag were heaped up. The Theissen mud result from generating of fly ash by means of the so called Theissen cleaning process. The Theissen mud was dumped into 10 artificial ponds with a total volume of some 100 Thousands m^3. Recently all these ponds are remediated by multy-layer covering according to the German regulations for chemical toxic waste management.

The slag contains mainly U 238 and Ra 226 in the range of 0.4 Bq/g to 2.0 Bq/g, whereas Pb 210 and Po 210 reaches about 10 Bq/g each in Theissen mud [1]. That is the result of the thermal processing due to the low volatility of uranium and radium and the high volatility of lead and polonium.

3 RE-USE OF COPPER SLAG

The use of the slag from copper smelting of the Mansfeld region (Saxony-Anhalt) have already a long tradition mainly as construction material. The hot glutinous slag was either heaped up or filled in a casting box to form bricks. A lot of roads and public places were constructed by means of these bricks, not only in this region but also everywere in Germany and middle Europe. Also some wave brakers at the North Sea coast are made from copper slag bricks. Nevertheless, the greatest portion of the slag is recently still heaped up.

The structure of copper slag is like glass with a high resistency against weather effects. The only radiological problem is rising up from the gamma dose rate of about 200 nSv/h to 400 nSv/h in dependance of the Ra 226 concentration whereas the emanation of Rn 222 is strongly limited due to the glass-like structure.

Because the recultivation of big copper slag heaps is impossible the re-use of the slag was considered as a practicable solution of the problem. Therefore allready in 1991 the German Commission on Radiological Protection (SSK) recommended the re-use of copper slag for the construction of roadbeds [6]. Nevertheless, the company which processes this material needs a licence from the Radiation Protection Authority based upon the Radiation Protection Ordinance (VOAS) of the former GDR. Furthermore, for the re-use of this material this authority had to grant a permission on the basis of the Order for re-use of contaminated materials (HaldAO). Both regulations remained their validity till 2001 on the territory of the former GDR. Since the implementation of the new Radiation Protection Ordinance (StrlSchV) in 2001 the permission for the re-use of the copper slag was redrawn by the State Authority of Saxony-Anhalt, although it would be possible if considering only the limit of the radionuclide concentration given in this new regulation. But the new Radiation Protection Ordinance is only applicable to recent work and not for residues resulting from past processing of such materials.

4 RE-USE AND DISPOSAL OF RESIDUES FROM OIL AND GAS EXTRACTION

Since a coupple of years different methods for re-use and disposal of sludge and scales from gas and oil extraction are applied or the licensing process is running. The preference of an option depends e.g. from the radioactivity level and the presence of mercury in connection with the changing legal grounds. Following, different options for re-use or disposal of contaminated scrap or separated scales are discussed.

4.1 Re-use or disposal of contaminated scrap

Untreated tubes could left in place. But, unfortunately that is not applicable for feed pipes due to restrictions by the German Mining Act.
Its dumping on common land fills, clay pits or holes from open pit mining was only possible (as long as the regulations from the former GDR were still in force) if the specific activity of the scales inside the tubes is lower than 0.2 Bq/g and mercury is absent. This option was not applied because its smelting was prefered due to economical reasons. With respect to the above mentioned maximum specific activity no restrictions for smelting exist.
Recently also higher contaminated scrap could be dumped on such places according to Annex XII part C of the StrlSchV if mercury is absent. But for such scrap with specific activity of the scales higher than 0.2 Bq/g the unrestricted smelting is not allowed. The dumping at land fills of low contaminated scrap with a total activity of the scales between 0.2 Bq/g and about 1 Bq/g was allready executed. But the portion of such tubes is to small to apply this option on a broader scale in connection with the expenditure of radiactivity measurements to control the maximum permissible specific activity.
During the last three years GRS worked out an option for the disposal of scrap poluted by both, natural radioactivity and mercury in an underground disposal site for toxic waste [7] basing on the principles of the StrlSchV in connection with the regulations for toxic waste management and the transportation of dangerous goods. This option is applicable for a cross activity of the scales up to 40 Bq/g. A great progress was achieved in licensing process till spring of this year. Now this process was interrupted by the Mining Authority of Saxony-Anhalt due to intervention by the owner of this underground disposal site which is a separate part of an operating potash mine.
Therefore huge amounts of scrap contaminated by both, radioactivity and mercury are recently piled up at storage areas of the oil and gas companies. At the moment, the only option is its restricted smelting by the Simpelkamp company having a licence for smelting of such scrap. This application of thos option is limited due to very high costs.

4.2 Re-use or disposal of separated scales

The scales can be separated from the pipes by means of sand blasting or high pressure water jet techniques. Sand blasting is prohibited in Germany since some years because the dose to workers resulting from inhalation of dust is unacceptable high.
In contrast, the application of high pressure water jet techniques becomes increasing importance. The remaining radioactivity of the cleand up tubes is lower than 0.1 Bq/g. Therefore the unrestricted re-use of such tubes should be possible but at the moment only its smelting is allowed.

For the re-use or disposal of the separated scales different methods are applied. The common method was the backfilling of the scales into the boreholes. Recently this method was stopped by the responsible Mining Authority due to stronger demands for the long term safety, i.e. for the exclusion of the migration of mercury into the groundwater. Nevertheless, some geological formations where oil and gas extraction takes place fulfil these conditions and backfilling takes place again.

The last option is directed towards the recycling of mercury in connection with the storage of the residues resulting from that process. This method concerns te demercurisation of sludge from oil and gas industry. Recently this method was modified for scales. According to [1] the recycled mercury is of highest purity. After the selectiv purification the sludge or the scales still contain the same specific activity as before. These residues - in case of sludge after partial dewatering – are mixed with a Geopolymer^{R} (high-alkali (K-Ca)-Poly(sialate-siloxo) binders) for immobilisation [7]. The sludge or the scales, that means waste, are going to be again a waste after demercurization, but

- on the one hand an important raw material (mercury) is extracted and on the other hand a high toxic substance is removed;
- simultaneously, hydrocarbons are removed ;
- the remaining radionuclides are safely encased for the long-term due to conditioning by means of Geopolymer$^{R;}$
- the storage of the immobilized residues in land fills or underground dump sites is possible in accordance with the legal frame conditions.

5 LEGAL FRAME CONDITIONS FOR RE-USE OR DISPOSAL OF TENORM

The above described methods for re-use or disposal of some TENORM are only applicable if they are in agreement with the legal frame conditions. That concerns not only the regulations on radiological protection but also those on recycling and storaging of common residues and waste as well as on the transportation of dangerous goods. In every case – except for the controlled smelting by Simpelkamp Co. – the precondition for the implementation of each practice is the release of the concerning residue from the radiological supervision according to § 98 of StrlSchV in connection with Annex XII, part A (kind of material) part B (maximum permissible specific activity), part C (maximum permissible specific activity of the total material of an landfill) and/or part D (keeping of the dose limit of 1 mSv/yr).

The procedure necessary for the release of such materials from radiological supervision is much more complicated than assumed, because the regulations for the different legal aspects are not well tuned. This will be demonstrated exemplary for the following two cases.

The Radiologial Protecton Autority can release such residues from supervision if the above mentioned canditions are fulfiled. On the other hand, in case of joint disposal with common waste the Autority which is responsible for common waste affairs must allocate a single disposal facility. But the owner of this facility can only accept such material after its release from radiological supervision. For that reason the most of licencing processes are not yet finally decided, especially if autorities from different German states are involved into this process.

A further problem is rising up from the regulations for transportation of dangerous goods. In Germany it is not allowed to store such radioactive waste and contaminated residues (TENORM) at disposal facility for toxic waste which are transported under the regulation for transportation of radiactive materials on roads. This option for disposal is interupted because the maximum permissible concentration of natural radinuclides for release from radiological supervision may be higher than the minimum specific activity according to the regulation on transportation of radiactive materials. Whereas according to the StrlSchV the release is based on the maximum specific activity of that nuclide with the higest activity, for transportation issues the sume of all long living radionuclides must be considered. For stady-state conditions this value is 100 Bq/g but for non-equilibrium conditions it depends from the portion of radioactive thorium isotopes having a 10times lower boundary limit than e.g. radium or lead isotopes. That results in a “flowing minimum permissible activity” for transportation as the following figure demonstrates.

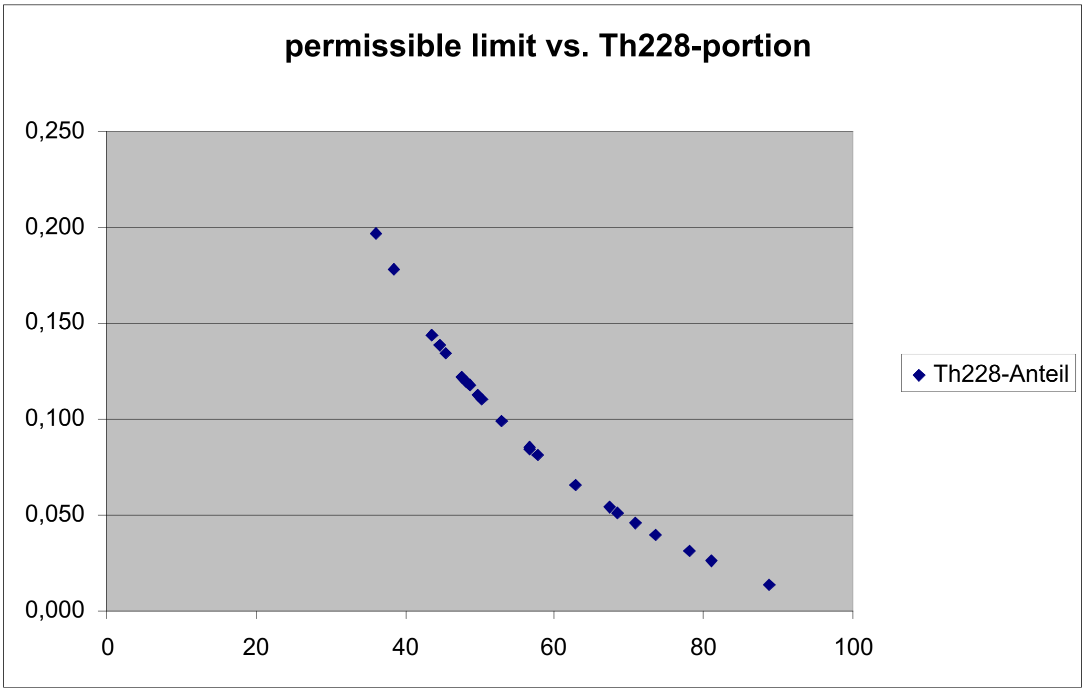

Figure 1: Minimum cross activity for release from transportation regulation in dependance of the portion of Th 228 against the portion of Ra 226, Ra 228, Pb 210 and Po 210 [8]
Nevertheless, the most of the above disussed problems are now solved or being on way.

6 SUMMARY AND CONCLUSIONS

- The most of TENORM can be released from radilogical supervision according to § 98 StrlSchV.
- The main problems which have to be solved during the licensing process arising from the superposition of different legal aspects which have to be taken into account.
- There is not only one preferred option for re-use or disposal of a special kind of TENORM, e.g. scales from oil and gas extraction but it depends from different factors as
  - level of the specific activity or
  - presence of chemical toxic substances.
- One grucial probleme needs still an answer. What´s with such material which must remain under radilogical supervision according to § 99 StrlSchV? Are these materials radioactive waste or not?

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