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Radioactive scales from a natural gas production facility in the Altmark region, Germany

D. Read, S. Black & S. Ceccarello
Enterpris, Universities of Reading and Aberdeen, UK
H.Weiss, M. Schubert
UFZ Centre for Environmental Research, Leipzig, Germany
Ch. Kunze
WISUTEC Wismut Umwelttechnik GmbH, Chemnitz, Germany
J. Grossmann
GICON GmbH, Dresden, Germany

ABSTRACT: Radioactive scale is widespread in oil and gas production facilities. The most common scale mineral is barite ($BaSO_4$), which incorporates radium isotopes by ionic substitution in the barite lattice, but other phases also occur. In the Altmark region of East Germany, crusts of metallic lead and mercury-lead compounds (mm to cm of size) have been found in both well tubing and surface installations of a gas field. The deposits with an approximate composition $HgPb_2$ have been tentatively named ‘altmarkite’. These early studies did not address the issue of natural radioactivity. Consequently, a more detailed program of chemical and mineralogical analysis was undertaken in an attempt to better understand the nature of the deposits and their mode of formation. Owing to the volume of contaminated plant accumulated over the past few years also handling, clean-up and disposal of the scales comes into the focus of interest. Different handling and disposal options for scales and radioactively contaminated plant exist. Any solution chosen for remediation of the studied site must conform to German and EU regulatory criteria and requires careful assessment of local environmental factors. However, the incidence of such Hg-Pb deposits could be much more widespread than is thought at present owing to the recent discovery of the ‘new mercury ore belt’ in Western Europe, which extends through Poland, East and West Germany, the Netherlands and the south of England.

1 INTRODUCTION

The Altmark region in the State of Sachsen-Anhalt, Germany hosts major gas production fields. The reservoir rocks are Lower Permian (Sachsen) sandstones and production wells can reach a depth of 3500 m. Formation waters are of NaCaMg-Cl and CaNaMg-Cl types with mineralization leading to dissolved solids around 360 g/dm^3 (Müller, 1990). The gas itself contains mercury at concentrations up to 4 mg/m^3.

Kaemmel et al. (1977) described lead and mercury-rich scales from installations at these gas fields. They identified a lead amalgam ($HgPb_2$) and tentatively gave it the mineral name ‘altmarkite’, subsequently rejected by the International Mineralogical Association (1980) on the grounds that the material may not be of natural origin but an industrial artifact. However, a naturally occurring lead amalgam of similar composition was discovered in a platinum-bearing Cu-Ni sulfide deposit from China and hence altmarkite was re-defined and accepted as a mineral in 1985 (Dunn et al., 1985). These early studies classified the scales and the encrusted tubes on which it forms as hazardous substances (or waste) owing to its chemical composition. They did not establish that the material is also highly enriched in radionuclides of the natural U-Th decay series. The present paper describes recent radiochemical and supplementary analyses, which suggest that altmarkite is more properly categorized as Naturally Occurring Radioactive Material (NORM).

2 SAMPLING

Samples were obtained from production well tubes at the Salzwedel-Peckensen field, Altmark, and date from 1988. Macroscopically, they comprise massive, apparently amorphous deposits with a pronounced metallic luster. The material is soft, friable (reported hardness values are 1.5-2 for altmarkite (Fleischer et al., 1979) and Pb-Hg (62.38%-32.62%wt) amalgam (http: // webmineral.com/ data/ leadamalgam. shtml) respectively) and easily cut with a scalpel. The color on a freshly polished surface is white-silver to grey. Darker areas (dark grey to black) are visible on some surfaces suggesting partial oxidation or possibly, local accumulation of different phases (Fig. 1).

3 EXPERIMENTAL

The mineralogy, bulk composition and γ-ray activity of the material have been determined. X-ray diffraction analysis (XRD) was used to characterize the mineralogy and the microcrystallinity of the samples (X-ray Diffractometer SIEMENS D5000). The bulk composition was determined by ICP-OES (Perkin Elmer Optima 3000 with AS90 Auto Sampler) after complete dissolution in HNO_3 solution. Five samples from both the surface and interior of the deposit were analyzed to assess homogeneity. Gamma (γ) activity was measured on a B5030 Canberra Broad Energy Germanium Detector (3800mm^2 active area) on the dissolved samples. Finally, a Scanning Electron Microscope (Jeol LV5900) equipped with an Oxford Instruments INCA Energy 400 microanalysis system attachment for Energy Dispersive X-ray analysis (EDX) was used to characterize the morphology and obtain compositional information. The latter includes an EDX trace for elemental analysis, elemental mapping and quantitative element determination on polished surfaces. Polishing was achieved through Focused Ion Beam-Secondary Ion Mass Spectroscopy (FEI-FIB200SIMS).

4 RESULTS AND DISCUSSION

The mineralogy of the material appears to be comparable to a synthetic tetragonal lead-mercury amalgam (serial number 39-0395 of the International Centre for Diffraction Data- 1601 Park Lane, Swarthmore, Pennsylvania, 19081-2389 U.S.A.). However, the strongest XRD lines at 2.77, 2.48 and 1.67Å are shifted slightly in terms of both, their position and relative intensity when compared to the main X-ray peaks from the reference sample, indicating some differences in composition and crystallography. The spectrum also shows other diffraction peaks (d=3.337, d=3.087), which correspond to quartz and lead oxide (PbO). The latter is represented by a rather broad peak, which is probably due to chemical interaction with mercury. Black areas are noticeable on the surface of the mineral indicating partial oxidation of metallic Pb to PbO. Overall, the Pb-Hg deposit analyzed in this study appears to give a very close match to the signature of tetragonal altmarkite (strongest XRD lines 2.78, 2.49 and 1.67Å), as reported by Fleischer et al. (1979). The bulk composition of the material is shown in Table 1. The deposit consists mainly of Pb and Hg with accessory Ba, Fe, S, Ca and Sr.

Table 1. Bulk composition determined by ICP-OES analysis (composition expressed as elemental wt%).

As	Ba	Ca	Cu	Fe	Hg*	Pb	S	Sr	Zn
0.06	0.28	0.09	0.04	0.13	37.7	61.48	0.14	0.06	0.01

* By difference on bulk, confirmed by spot analysis.

The mercury content determined initially by Atomic Absorption, after complete dissolution in HNO_3, ranged between 20-40% (wt/wt). Likely sources of error were the volatility of Hg, which can be released during HNO_3 digestion and the high dilution factor needed. The composition was confirmed, therefore, by quantitative EDX analysis of a polished surface (Fig. 2).

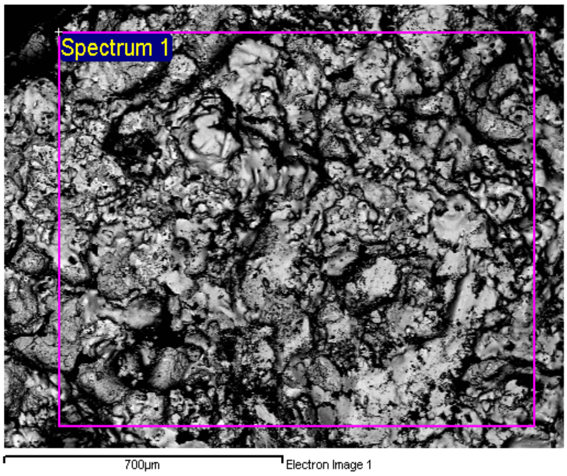

Figure 1: SEM image of the Hg-Pb deposit.

The sample is characterized by a high degree of heterogeneity on unpolished surfaces. Amalgams with compositions ranging from 5.1 – 94.3 to 90.6 – 8.9 (Hg-Pb wt%) were found over a wide area of the sample through EDX microanalysis (Fig.3). Dark inclusions were identified on the external surface, containing primarily Ba, Sr, Ca, S, O and Pb. These components were absent in analyses of polished surfaces and, hence, it is reasonable to suspect the presence of a surface film in which altmarkite loses its microcrystalline structure and within which other mineral phases, such as $(Ba,Sr)SO_4$, $CaCO_3$ and PbO are deposited. This aspect merits further investigation.

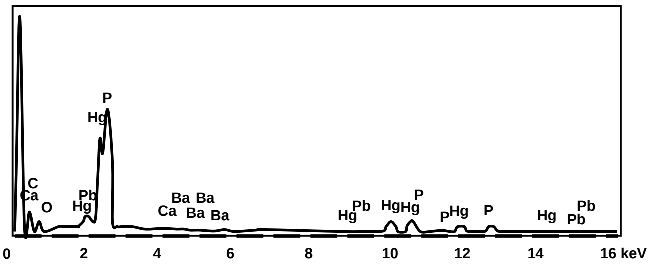

Figure 2: EDX trace of the area highlighted in Figure 1 (1.19mm^2).

The Sample contains Naturally Occurring Radioactive Material (NORM) from the ^{238}U (^{226}Ra, ^{214}Bi, ^{210}Pb) and ^{232}Th (^{228}Ra, ^{212}Pb) decay series. The Pb-Hg deposit is characterized by significant activity with regards to all the radionuclides cited above (excluding ^{228}Ra). ^{210}Pb is the main radionuclide present in the mineral with an activity of 4285 Bq/g. Five different areas of the Hg-Pb deposit were monitored (samples analyzed after complete dissolution in HNO_3). The value quoted represents the mean though ^{210}Pb appears to be distributed homogeneously within the regions sampled.

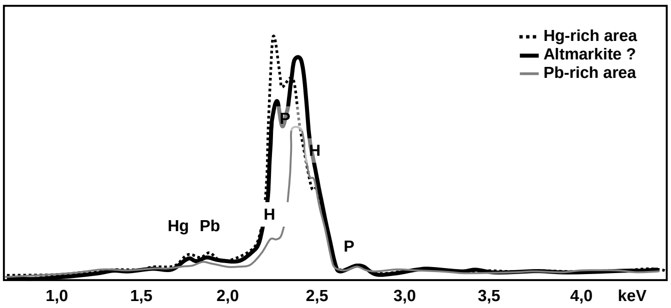

Figure 3: Overlaid EDX traces of three Pb-Hg surface amalgams showing compositional variation.

Owing to the volume of contaminated plant accumulated over the past few years, handling, clean-up and disposal of the scales poses a number of technical and economic problems. Any solution chosen for remediation must conform to German and EU regulatory criteria and requires careful assessment of local environmental factors.

Different handling and disposal options for scales and radioactively contaminated plant exist (Read et al., 2004). The first issue to resolve is whether the plant has significant residual value (e.g. specialized stainless steel equipment) or can be disposed of directly. Cleaning options are invariably costly and can lead to relatively high radiation exposure for workers. In the case of altmarkite, problematic residues would require solidification and, almost certainly, prior processing to remove mercury. Removal of mercury from the $HgPb_2$ is technically feasible though the materials remaining are still hazardous and fall within the ambit of NORM waste. In those cases where cleaning is the only accepted option, owing to environmental, regulatory or economic constraints, a geopolymer comprising an alkali-activated aluminosilicate matrix, has been developed to encapsulate scale material recovered by high-pressure water jetting. The matrix has proven long-term stability and has been accepted by the German regulators for the disposal of NORM wastes in municipal landfills.

Should a decision be made not to clean the plant, available options essentially reduce to smelting and direct disposal. Smelting has the advantage of recovering steel value, but the potential for cross-contamination during steel production is critical. Limits to throughput capacity may be set too low for this solution to be viable. Direct disposal is simpler with fewer problems regarding capacity. National legislation defines clearance and exemption levels below which NORM wastes can be disposed of in ordinary or industrial landfills. For example under the German Radiation Protection Act, provided the specific activity of the combined steel and attached scales does not exceed 50 Bq/g, it can be consigned to this route. In this case, the challenge is finding a separation method that allows the amount of waste requiring treatment to be minimized. Semi-automatic activity measurement equipment with high throughput has been developed for this purpose. It incorporates automated recording and database management for large quantities of wastes ensuring traceability of individual items, if required by regulatory authorities. Results for material from the Altmark region indicate that only 1 – 2% of the total amount of steel scrap requires special treatment (smelting or cleaning); the remainder can be disposed of to industrial landfills.

The results of the characterization study and the technology applied to remediation are applicable to other industrial sites contaminated by NORM materials.

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