

## 4.64.P03

### Characterisation of radioactive Hg-Pb deposits found in natural gas production installations

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Radioactive scale is widespread in oil and gas production. The most common scale mineral is barite (BaSO<sub>4</sub>), which incorporates radium by ionic substitution but other phases also occur. In the Altmark region, Eastern Germany, crusts of metallic lead and mercury-lead compounds (mm to cm size) have been found in well tubing and surface installations in the Rotliegend gas field [1]. These crusts, approximately HgPb<sub>2</sub>, have been tentatively named 'altmarkite' [2].

Early studies did not address the issue of natural radioactivity. A more detailed chemical and mineralogical characterization has refined the nature of the deposits and their mode of formation. X-ray diffraction patterns closely match that of altmarkite with strongest peaks at 2.77, 2.48 and 1.67. Bulk composition (ICP-OES, Inductively Coupled Plasma Optical Emission Spectroscopy) shows mean Pb content of 61.5% (wt%), with trace Ba (0.28%), Ca (0.09%), Fe (0.13%), Sr (0.06%) and S (0.14%). Mercury, determined by difference, would therefore be ~ 37 wt% which was confirmed by quantitative SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-ray analysis) on a freshly polished surface obtained through FIB-SIMS (Focused Ion Beam-Secondary Ion Mass Spectroscopy). Analysis of unpolished external surface showed co-existence of Hg-Pb amalgams ranging from 5.1-94.3 to 90.6-8.9 (Hg-Pb wt%).

Radiological properties were studied by  $\gamma$ -spectrometry. Naturally occurring radionuclides from the <sup>238</sup>U (<sup>226</sup>Ra, <sup>214</sup>Bi, <sup>210</sup>Pb) and <sup>232</sup>Th (<sup>228</sup>Ra, <sup>212</sup>Pb) decay series were observed. Fractionation was extreme with unsupported <sup>210</sup>Pb at activities  $\leq$  4285 Bq/g, greatly in excess of parent <sup>226</sup>Ra. The important and volatile  $\alpha$ -emitter, <sup>210</sup>Po, must be present at similar levels but whether it occurs in excess of <sup>210</sup>Pb when first formed remains to be confirmed.

Results suggest the material to be 'altmarkite'. Other phases (Ba-, Ca-, Cd-, Bi-rich) were <1% and small amounts of PbO, mostly on the external surface, were recognisable by XRD. Such Hg-Pb deposits could be more widespread than currently thought owing to the recent discovery of the 'new mercury ore belt' in Western Europe, extending from Poland to south England [3].

#### References

- [1] Kaemmel et al. (1978) *Agew. Geol.* **24** 90-96.  
[2] Fleischer et al. (1979) *Amer. Miner.* **64** 652-679.  
[3] Ozerova N.A. (1983) *J. Geol. Rev.* **25(9)** 1095.

## 4.64.P04

### Experimental sorption of Cs<sup>+</sup>, Ni<sup>2+</sup> and Eu<sup>3+</sup> onto a montmorillonite from 25 to 150°C

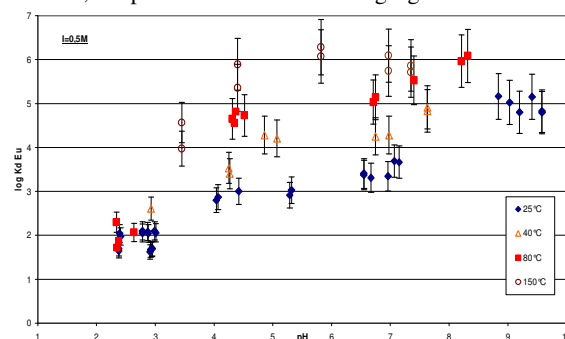
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Metal sorption onto clay minerals is well documented, at least at room temperature. However, data relative to the sorption dependence on temperature are very few.

The present study is devoted to the temperature effect (25-150°C) on the sorption of Cs<sup>+</sup>, Ni<sup>2+</sup> and Eu<sup>3+</sup> onto a montmorillonite, as a function of pH and ionic strength. Such data are important for the radioactive waste management, since temperature up to 50°C are predicted in the nearby storage area until 1000 years. Our experiments were performed in PTFE containers at 25, 40 and 80°C, or in PTFE liner inserted in a hydrothermal reactor at 150°C. 100 ppb of each element were added to previously equilibrated suspensions. After 3 days of reaction time, the aqueous phase was isolated by centrifugation (25 and 40°C) or filtration (80 and 150°C). Apparent distribution coefficients (K<sub>d</sub>) were deduced from the chemical analysis of the supernatant or filtrate. As an example, the results obtained for Eu<sup>3+</sup>, at I=0.5M, are presented on the following figure.



The results are similar for Ni<sup>2+</sup>: at pH=7 and I=0.5M, log K<sub>d</sub> increases by a factor 1.5 when temperature increases from 25 to 150°C. Moreover, the temperature effect increases with increasing ionic strength, especially in the medium pH range (4-8).

We report below apparent thermodynamic properties for the sorption reactions, estimated from the data at pH=7. Endothermic reactions were observed for Ni<sup>2+</sup> and Eu<sup>3+</sup> sorption, which are likely complexed at the edge of the particles, and exothermic reaction for Cs<sup>+</sup> which is likely in the exchange sites.

	Cs <sup>+</sup>	Ni <sup>2+</sup>	Eu <sup>3+</sup>
$\Delta_r H$ (kJ.mol <sup>-1</sup> )	-	33	34
$\Delta_r S$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )	-	164	208