

## II/1 ORIGIN AND ENCOUNTER OF $^{210}\text{Pb}$ IN E&P FACILITIES

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### Abstract

Under gas/oil production conditions, lead precipitates are found which have been reported to contain  $^{210}\text{Pb}$  from the  $^{238}\text{U}$  series. Here  $^{210}\text{Pb}$  is 'unsupported' - i.e. its concentration can neither be explained from  $^{226}\text{Ra}$  contributions in Low Specific Activity (LSA) deposits, nor from  $^{222}\text{Rn}$  concentrations in natural gas - and it is transported together with stable (non-radioactive) lead carrier. An analysis of the morphology and composition of the precipitates shows the presence of three main categories: a) thin, heterogeneous crusts containing lead and lead compounds, together with other scales; b) homogeneous (massive) lead deposits; c) loose precipitates. The stable lead isotope composition of these precipitates is very similar and skewed towards lead of radiogenic origin from the  $^{238}\text{U}$  series. In order to determine the origin of the lead and to understand the deposition mechanism, reservoir material has been studied in detail, as well as various deposits found in oil- and gas Exploration and Production (E&P) facilities.

### Introduction

The encounter and distribution of (Technologically Enhanced) Naturally Occurring Radioactive Material ((TE)NORM) in various product and waste streams from the gas and oil E&P industry has been described in an earlier paper<sup>1</sup>. In literature, most attention has been paid to radium containing LSA scales. For these scales, a great similarity exists with common 'conventional' (calcium, barium and strontium sulphate and carbonate) scales. Both the mechanism for the transport of radium from the reservoir to the topside facilities with the produced brine as well as the formation of radium ( $^{226}\text{Ra}$  from the  $^{238}\text{U}$ -series and  $^{228}\text{Ra}$  from the  $^{232}\text{Th}$ -series) containing scales is fairly well understood and documented. Next to  $^{226}\text{Ra}$  and  $^{228}\text{Ra} / ^{224}\text{Ra}$ , also  $^{210}\text{Pb}$  can (sometimes) be detected in these scales. This lead isotope originates almost exclusively from in-situ decay of  $^{226}\text{Ra}$  in the scale; since the emanation factor for  $^{222}\text{Rn}$  in these scales is very low<sup>2</sup>, the age of the scale can be calculated from the  $^{210}\text{Pb} / ^{226}\text{Ra}$  ratio in the scale.

The deposition of  $^{210}\text{Pb}$  in Natural Gas Liquids (NGL) fractionating units, such as de propanisers and de-butanisers in which a concentration of the noble gas radon can take place, is also well known: after several years of operation "invisible"  $^{210}\text{Pb}$  deposits are found in some plants with very high activity concentrations<sup>3</sup>. These deposits originate from the decay of  $^{222}\text{Rn}$ , which has a fairly long residence time in the installations. The same phenomenon has been observed for gas transport systems<sup>4</sup>, in which the residence time of the gas is also in the order of days. The origin as well as the mechanisms responsible for transport and deposition of  $^{210}\text{Pb}$  are fairly well documented and understood<sup>5</sup>.

In the last few years attention has been focused on scales containing 'unsupported'  $^{210}\text{Pb}$ <sup>6,7</sup>. In these scales, which are almost exclusively encountered in gas producing facilities, no or too little  $^{226}\text{Ra}$  is present to account for the observed  $^{210}\text{Pb}$  activity. In marked contrast to the deposits found in natural gas transport, storage and fractionating units,  $^{210}\text{Pb}$  is here always accompanied by stable (i.e. non-radioactive) lead, which acts as the 'carrier' for the radioactive isotope. The origin of this lead, the mechanism for its transport and its deposition are relatively poorly understood. In this paper, examples of unsupported  $^{210}\text{Pb}$  containing compounds are presented, together with the chemical composition and the deposition mechanism. Preliminary results on the characterisation and deposition of some of the scales have been reported earlier<sup>8</sup>. The origin of lead and the mechanisms for the transport of lead from the reservoir to the site of deposition will be discussed elsewhere<sup>9</sup>.

### Encounter and Analysis of Lead Containing Deposits

In Figure 1, the spots where 'unsupported' lead deposits have been found in an E&P gas producing installation are indicated with the radiation symbol.

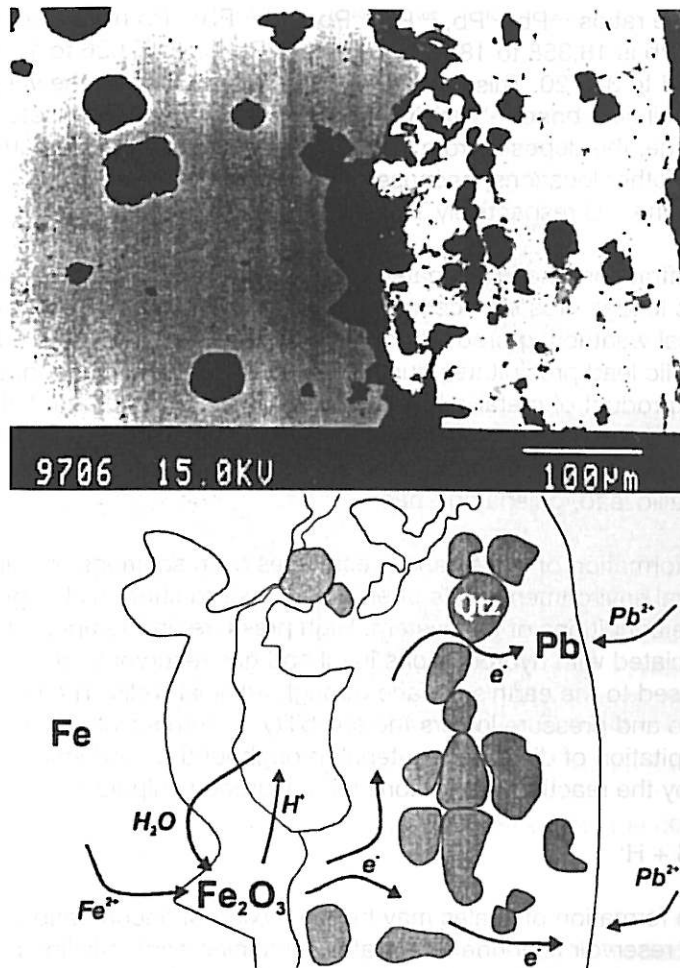


Figure 2: SEM photograph and a schematical presentation (partially enlarged area) demonstrating the electrochemical deposition of elemental lead on iron tubing

We have studied scale covered steel parts from gas producing equipment and have found that this mechanism might also be responsible for the deposition of elemental lead. Iron is locally dissolved, causing corrosion of the steel. Dissolved iron produces goethite and/or haemite, forming an oxidation rim on the steel surface. Metallic lead may precipitate onto the oxidation rim. The porous nature of the oxidation rim allows the continuous supply of water to the steel, enhancing the dissolution of the iron. Electron transport through the oxide layer and metallic rims enables the latter rim to grow steadily on the outside, i.e. on the inner surface of process equipment. This mechanism is schematically shown on a drawing after a Scanning Electron Microscope (SEM) picture from a recent deposit.

Alternatively, uniform corrosion over the entire length of the steel pipe may induce a steady flow of electrons towards one site, concentrating the precipitation of metallic lead on a very localised area. In this way, deposits can grow large very rapidly (as has been observed in several E&P facilities); even clogging of a whole pipe has been reported<sup>17</sup>.

## CONCLUSIONS

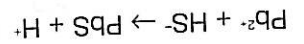
A detailed study onto the encounter of <sup>210</sup>Pb containing scales in the E&P industry has shown that for their deposition three mechanisms may be operative:

1. In-situ decay of <sup>222</sup>Rn, provided that the radon has a sufficient long residence time in the facilities. These deposits are encountered mostly in low-temperature fractionating units; in storage tanks and in transport equipment.
2. In-situ decay of <sup>226</sup>Ra, present in earth alkaline scales. These deposits can be encountered at any position where 'ordinary' gas- and oil-field scaling takes place.

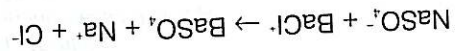
The lead stable isotope ratios  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  have also been determined. The range for  $^{206}\text{Pb}/^{204}\text{Pb}$  is 18.358 to 18.791; for  $^{207}\text{Pb}/^{204}\text{Pb}$  from 15.626 to 15.690 and for (world-wide) ratios in oil field brines<sup>10,11</sup> and with the average crustal lead isotope ratios<sup>12</sup>. Even within this narrow range, the deposits from location 'A' can clearly be distinguished from the deposits found at the other locations, because of the relatively low abundance of  $^{206}\text{Pb}$  and  $^{208}\text{Pb}$  (radiogenic lead from the  $^{238}\text{U}$  respectively Th series).

As shown by X-ray diffraction, the investigated scales contain different lead minerals; in many samples also metallic lead is present, accompanied by lead oxides and hydroxides. These latter compounds are typical weathering products of metallic lead<sup>13</sup> and are believed to result from the oxidation of metallic lead precipitates during and after sampling. Laurionite is reported to be a common corrosion product of metallic lead in a moist, salty environment<sup>14</sup>. It is not unlikely, that the required conditions have been encountered during e.g. cleaning operations prior to sampling. It can therefore be concluded that initially only three NOR-containing minerals have been deposited: metallic lead, galena and barite.

Scale formation The formation of scales and precipitates from solutions of salts is a common phenomenon in natural environments. It is often a response to sudden changes in the temperature and / or pressure conditions of the system. High pressure and temperature brines, for instance brines associated with hydrocarbons in oil and gas reservoirs, quickly become supersaturated when released to the earth's surface through artificial wells. The instantaneous decrease of temperature and pressure lowers the solubility of both solids and gases in the aqueous phase, causing precipitation of dissolved material throughout the production system, e.g. the formation of galena by the reaction of lead ions with hydrogen sulphide<sup>15</sup>

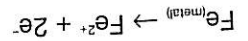


Other reasons for the formation of scales may be the mixing of 'incompatible' waters. Examples include the mixing of reservoir (chloride rich) water containing earth alkaline metal ions with injected (sulphate rich) water, which leads to the precipitation of barite<sup>16</sup>

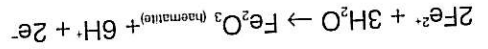
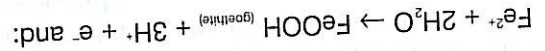


Initially, production from new fields / wells may contain relatively small amounts of water, but it is common that the water production gradually increases with ageing of the field. Scale formation also increases with an increasing water cut.

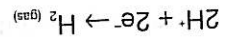
The deposition of elemental lead (and the formation of reaction products), containing 'unsupported'  $^{210}\text{Pb}$ , can not be explained by the above mechanism based on the sequence; 'supersaturation'  $\rightarrow$  nucleation  $\rightarrow$  mineral formation'. The deposition of elemental lead in E&P installations can be caused by the corrosion of steel from installations. The corrosion of iron in aqueous media is an electrochemical process, by which iron is dissolved according to the reaction:



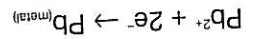
Dissolved iron may further be oxidised by water, forming goethite or haematite by:



In a reducing aqueous environment (e.g. a natural gas system), in the pH range from 3.5 to 6, the electrons may react with hydrogen ions, leading to the generation of hydrogen gas:



If dissolved lead is present in the system, a competing reaction might be:



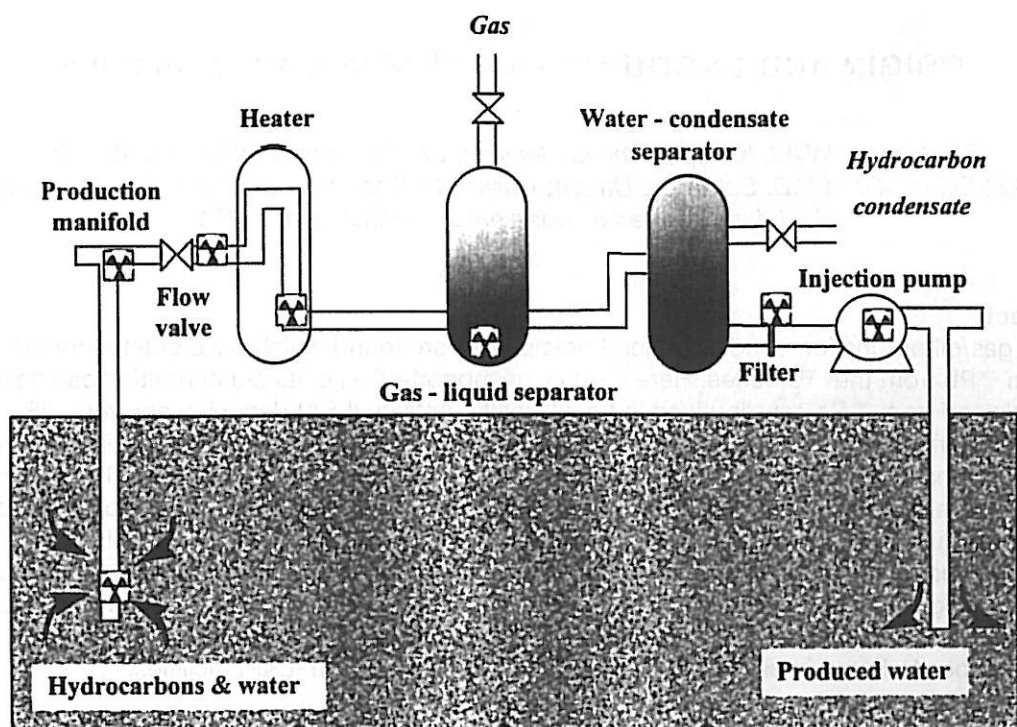


Figure 1: Schematic view of a natural gas production installation with the collection points of lead scales

In Table 1, the composition, the  $^{226}\text{Ra}$  and  $^{210}\text{Pb}$  activity concentrations, the collection point and the scale morphology are summarised.

Table 1: Encounter of Unsupported  $^{210}\text{Pb}$  Deposits at various E&P Production Locations

Prod. Location	Point of collection	Mineralogy	Pb (%wt)	$^{210}\text{Pb}$ (Bq/g)	$^{226}\text{Ra}$ (Bq/g)
A	Inlet production manifold	Ba, Ga, Sph	14	775	2840
	Outlet heater	Ba, Ga, Sph	n.d.	380	1516
	Inlet gas - liquid separator	Ba, Ga, Sph	3	57	184
	Inlet gas - liquid separator	L, Ba, Ga, Hy, Sph	10	1360	2203
	Inlet gas - liquid separator	Lo, Ba, Sph	55	605	746
	Inlet gas - liquid separator	L, Ba, An, Sph	60	1561	3016
	Outlet gas - liquid separator	Lo, Ba, An, Sph	85	780	1087
B	Tubing	Lo, Sph	n.d.	390	< d.l.
	Tubing, bottom of well	L	90	348	< d.l.
	Tubing	L, Ga	n.d.	348	< d.l.
C	Tubing	L, Lo	90	685	< d.l.
D	Tubing	L	93	1590	< d.l.
E	Outlet production manifold	Ga, Ba, Sph, Ca	6	307	695
	Outlet production manifold	Ga, Ba, Sph	n.d.	307	695
F	Flow control valve	L	85	380	< d.l.
	Production water filter	L, Ga, Lo, Hy	27	n.d.	n.d.
	Production water filter	L, Ga, Lo, Hy	41	271	< d.l.
	Water injection pump	L, Lo	85	288	< d.l.
G	Flow control valve	Lo	85	950	< d.l.
H	Gas - liquid separator	La, Lo	48	860	< d.l.
I	Tubing	Lo	n.d.	204	2

Legend: n.d.: not determined; < d.l.: below detection limit; L: elemental lead [Pb]; Lo: lead oxides [e.g. PbO, PbO<sub>2</sub> and Pb<sub>2</sub>O<sub>3</sub>(OH)<sub>4</sub>]; Ba: barite [BaSO<sub>4</sub>]; Ga: galena [PbS]; Hy: hydrocerussite [Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]; Sph: sphalerite [ZnS]; An: anhydrite [CaSO<sub>4</sub>]; Ca: calcite [CaCO<sub>3</sub>]; La: laurionite [Pb<sub>2</sub>Cl<sub>2</sub>(OH)<sub>2</sub>]

3. Transport of 'unsupported'  $^{210}\text{Pb}$ , together with non-radioactive 'carrier lead' with reservoir fluids. Elemental lead is precipitated by an electrochemical reaction; in the case of galena supersaturation might be responsible for its deposition. A fundamental understanding of the transport and deposition mechanisms is essential for the development of techniques for the prevention of this type of TENORM deposits in the E&P industry.

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