Some problems concerning determination of barium in mine waters of Upper Silesia (Poland)

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Abstract Insoluble precipitates in mine waters of coal mines in Upper Silesia (Poland) contain mostly barium sulphate and are characterized by varying granulation. These solid-phase deposits precipitate under intensive flowing and mixing conditions in mine workings and pipes pumping mine waters to the surface. They contain up to 10–15 % of small granulation less than 0.45 mm. Using recommended procedure to analyze barium in mine waters, both the soluble barium ion and the insoluble forms with grains from 0.1 to 0.45 mm are determined. We recommend using membrane filters with pore size less than 0.1 mm.

Keywords Mine waters, Upper Silesia, Barium Sulphate, Mine deposits, solid phases

Introduction

Natural mine waters of various origin and chemical composition flow into coal mines of Upper Silesia in Poland. Chemical composition of these waters results from natural (geogenic) hydrogeochemical processes and anthropogenic activities linked to the mining industry, causing differences in the content of barium and sulphate (VI) ions. In natural mine waters of the Upper Silesian Coal Basin concentrations of barium reach up to 2910 mg/dm^3 and of sulphate (VI) up to 8170 mg/dm^3 (*e.g.* Pluta 2005, 2011). In some coal mines waters with different contents of these compounds are mixed in the mine workings and insoluble precipitates, suspensions, colloids or mineral deposits are formed.

Analysis of barium and other micro-components in mine water consists of determination of the soluble form, *i.e.* barium ions (Nielsen 1991; Standard Methods 1989; Ordinance of the Minister of Environment 2006). According to Polish Law, analytical methods appropriate for groundwater and for mine water drained into surface waters can be used for this purpose. All mandatory analytical methods require water samples to be filtered with membrane filters with pore size 0.45 mm.

This paper presents results of the studies of the barium insoluble forms (mineral deposits, solid phases) precipitated in mine waters and pipes of mine-water transporting systems in coal mines of Upper Silesia.

Analytical methodology

Water samples were taken from mine workings of the Krupiński and Zofiówka coal mines, in which precipitation of barium takes place. Samples of mine water from Krupiński mine were taken and barium precipitated with sodium sulphate in the laboratory. The precipitation was variously conducted with the stirrer operating at 120 rotations per minute, by shaker, by hand mixing and without stirring.

Solid-phase deposits precipitated in mine waters and transportation systems were analyzed for granulation and chemical composition. Granulation measurements were performed employing a laser granulometer. The method allows determination of grains with size varying from 0.05 to 900 mm. Chemical composition of the insoluble forms was determined by sequential X-ray fluorescence (WD XRF) with wavelength dispersion using the

PRIMUS II spectrophotometer. Photographs of solid-phase deposits precipitated from mine waters were taken using the microscope at 10 and 110 times enlargements.

Results

Chemical composition of mineral deposits and solid phases precipitated in mine waters

Solid-phase deposits occur during mixing of the barium-containing natural mine waters flowing out of the Carboniferous strata, waters containing sulphate (VI)), waters removed from various mining technologies and the added sodium sulphate. These insoluble forms containing up to 53 % of barium occur mainly in mine waters flowing in mine workings, galleries and in pipes through mining floors up into the surface. They contain: $BaSO_4$, $CaSO_4$, $MgSO_4$, $SrSO_4$; or $BaSO_4$, $CaSO_4$, $SrSO_4$; or $BaSO_4$, $SrSO_4$; but mostly barium sulphate. For example, a typical deposit consists of $BaSO_4$ (94.1 %), $CaSO_4$ (3.3 %) and $SrSO_4$ (1.6 %) or $BaSO_4$ (86.4 %) and $SrSO_4$ (7.8 %). The varying chemical composition of insoluble forms results from different chemical compositions and origins of natural mine waters of the Carboniferous strata (*e.g.* Różkowski *et al.* 2004; Pluta 2005, 2011).

Granulation of solid phases precipitated in mine waters flowing in the mine workings

The histogram of granulation of the solid phase in mine water of the Krupiński coal mine is shown in Fig. 1. Like others, these insoluble forms have precipitated in mine waters flowing in the mine workings. They consist of two fractions: one with the size ranging from about 0.1 to 1.0 mm and the other with sizes from about 5 to 300 mm. The dominant fraction has the higher granulation. The solid phase also contains grains with size less than 0.45 mm.

In order to explain the differences in granulation the process of barium precipitation in mine water from Krupiński coal mine was studied under various types of mixing in the laboratory.

Granulation and appearance of the deposit precipitated in mine water under intensive mixing with sodium sulphate (stirrer)

Precipitation of barium and other ions in mine water using sodium sulphate was conducted with a stirrer operating at 120 rotations per minute. The size of grains of the resulting deposit was measured. The histogram of the granulation and appearance of the deposit are depicted in Fig. 2. It is evident that two fractions dominate: one with grain size from 0.1 to 1.0 mm and the other from a few to about 30 mm. The latter fraction is more abundant.

The deposit contains about 15 % grains smaller than 0.45 mm in diameter.

Granulation and appearance of the deposit precipitated in mine water under intensive mixing with sodium sulphate (shaker)

Fig. 3 displays the histogram of granulation of the deposit precipitated in mine water under intensive mixing with sodium sulphate in the shaker. Similar to the previous case, the histogram shows two fractions, with granulation in the range from 0.1 to 1.0 mm and from a few to about 30 mm. The external appearance

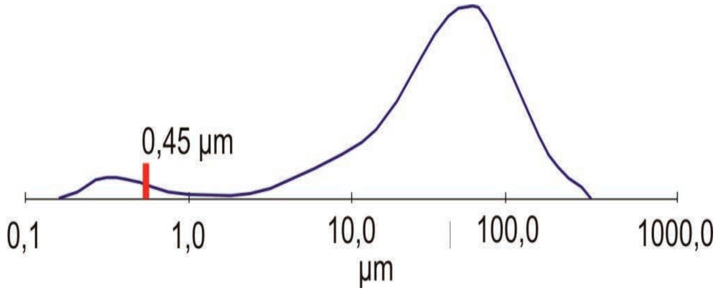

Fig. 1 *Histogram of granulation of the solid phase precipitated in mine water flowing in mine workings*

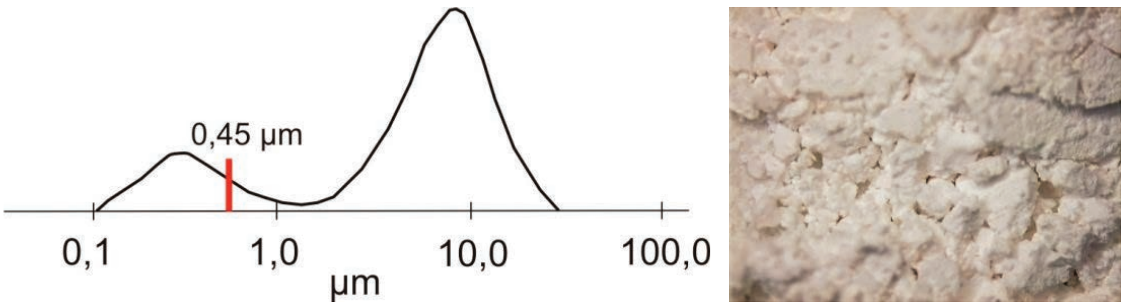

Fig. 2 *Histogram of granulation and appearance of the deposit precipitated in mine water under intensive mixing with sodium sulphate (stirrer)*

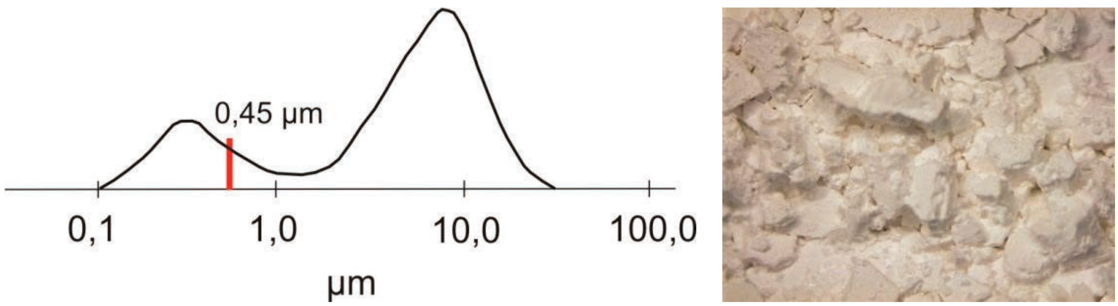

Fig. 3 *Histogram of granulation and appearance of the deposit precipitated in mine water under intensive mixing with sodium sulphate (shaker)*

of this deposit is also similar to the previous one.

Granulation of the deposit precipitated from mine water under gentle mixing with sodium sulphate (manual mixing)

The deposit precipitated under a few minutes of gentle, manual mixing shows the granulation without any dominant fraction (Fig. 4). The fraction of grains less than 0.45 mm is small. Granulation reaches up to approximately 800 mm.

Granulation and appearance of the deposit precipitated in mine water after adding sodium sulphate without mixing

The deposit obtained without mixing shows granulation in the range from about 50 to 1000 mm (Fig. 5), with the majority of the deposit in the range above 100 mm. This deposit does not contain grains with size less than 0.45 mm.

Granulation and appearance of the solid phase precipitated in the pipe filled with mine waters

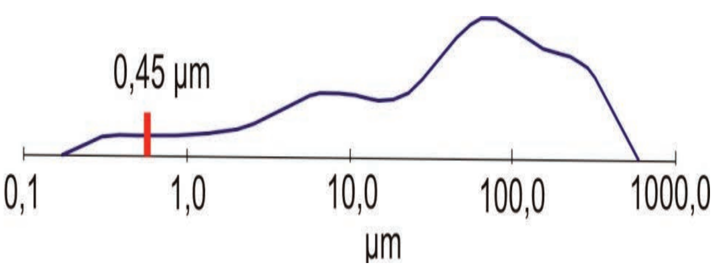

Fig. 4 *Histogram of granulation of the deposit precipitated from mine water under gentle mixing with sodium sulphate (manual mixing)*

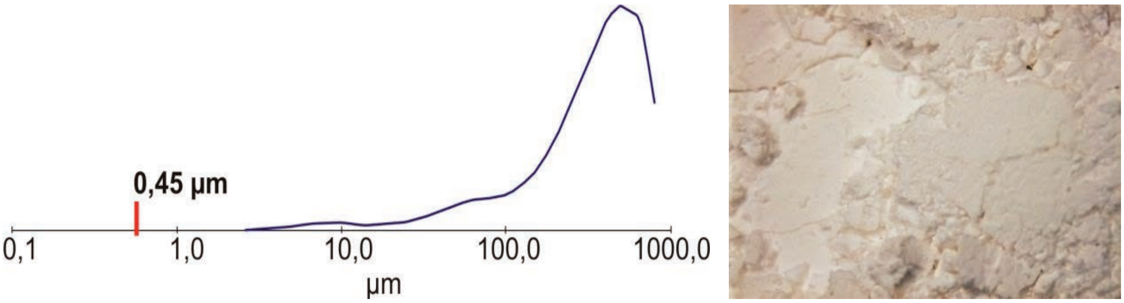

Fig. 5 *Histogram of granulation and appearance of the deposit precipitated in mine water after adding sodium sulphate without mixing*

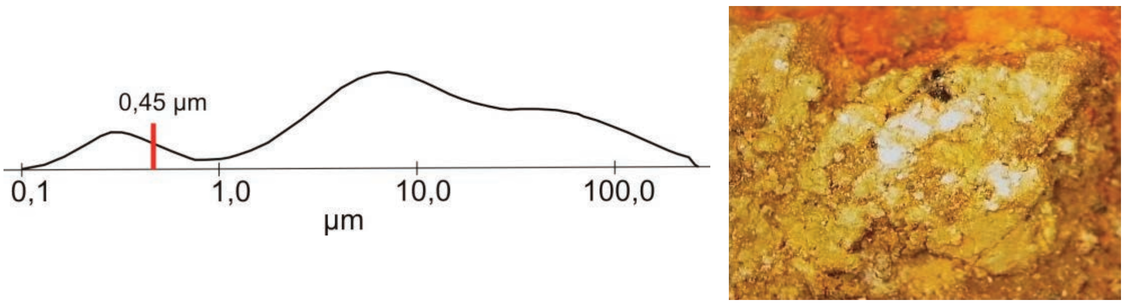

Fig. 6 *Histogram of granulation and appearance of the solid phase precipitated in the pipe filled with mine waters flowing from the underground sedimentation tank*

flowing from the underground sedimentation tank

Granulation of the solid phase precipitated in the pipe filled with mine waters flowing from the underground sedimentation tank toward the pump moving water to the surface is characterized by three ranges: from 0.1 to 1.0 mm; from a few to about 30 mm; and above 30 mm (Fig. 6). The fraction from few to 30 mm is the majority. The contribution of grains less than 0.45 mm is about 10 %.

Granulation of the solid phase precipitated in the pipe with water pumped out into the surface

Solid phases precipitated in the pipe in which mine water was pumped out into the sedimentation tank on the surface are characterized by granulation similar to the deposits formed in the laboratory under intensive mixing. Two fractions are present: from 0.1 to 1.0 mm and from a few to approximately 40 mm (Fig. 7). The solid phase contains about 10 % grains with the size less than 0.45 mm.

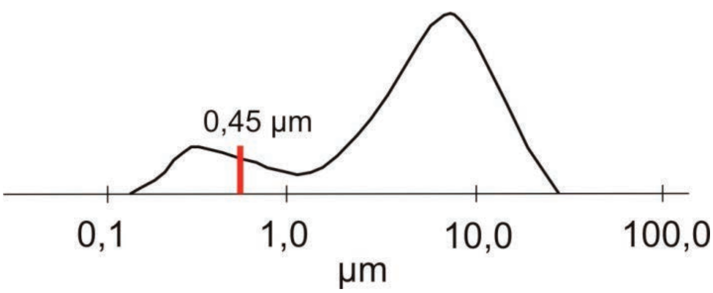

Fig. 7 *Histogram of granulation of the solid phase precipitated in the pipe with water pumped out into the surface*

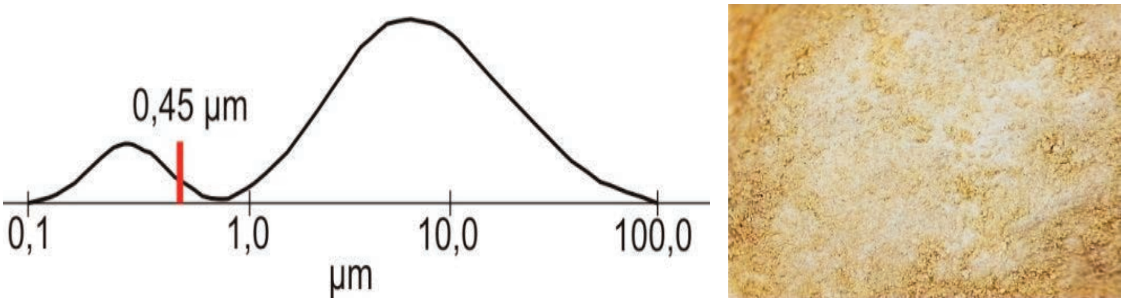

Fig. 8 *Histogram of granulation of the deposit precipitated in the pipeline of the Olza Collector*

Granulation and appearance of the solid phase precipitated in the pipeline of the Olza Collector

Water pumped up out of the mine flows into the sedimentation tank on the surface, from which after a few days (about 3–5) it is pumped into the Olza Collector pipeline carrying mine water into the Oder river. The histogram of the granulation and the appearance of the solid phase precipitated in the pipeline of the Olza Collector are depicted in Fig. 8. This solid phase contains two fractions of granulation: from 0.1 to 1.0 mm and from 1.0 to almost 100 mm. The contribution of grains less than 0.45 mm is about 15 %.

Interpretation and summary

Studies of solid phases and mineral deposits precipitated in mine waters of coal mines in the Upper Silesia (Poland) show variability of their composition and granulation. They contain mostly barium sulphate and are characterized by varying granulation. Two fractions of the deposits precipitated in mine waters mixed with sodium sulphate – one from 0.1 to 1.0 mm, and the other from a few to approximately 100 mm – are formed under intensive mixing of mine waters. Similarly, two ranges of granulation have been found in the solid phases precipitated in mine waters flowing in mine workings, in pipes with mine waters being pumped out into the surface, and in the Olza Collector pipeline. Lower mixing speed favors the deposit with larger grains and sometimes continuous granulation up to several hundreds of mm.

All solid phases and deposits in coal mine waters are characterized by up to 20 % small granulation from about 0.1 to 1.0 mm. This fraction also contains particles of less than 0.45 mm diameter. Solid phases from intensively flowing mine waters contain about 15 % of grains less than 0.45 mm. Using the recommended procedure to analyze barium in mine waters, both the soluble barium ion and the insoluble forms with grains from 0.1 to 0.45 mm are determined. Changes of the granulation of deposits and solid phases depend on the speed of the flowing waters. Therefore, it is highly recommended to use membrane filters with pore sizes less than 0.1 mm when barium in mine waters is to be determined.

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