

Removing barium from saline waters in coal mines of the Upper Silesia (Poland)

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Abstract Natural mine waters in the Upper Silesian Coal Basin (Poland) frequently exhibit high salinity and contain barium. Waters with this element discharged from coal mines cause contamination of water transportation systems, surface waters and their sediments. Therefore, purification of mine waters from barium is an important mining and ecological task in the Upper Silesia. This paper presents various methods applied in coal mines since the 1990s aimed at reduction of barium content in mine waters. Majority of these methods is an example of the most favorable elimination of contamination at the point of origin, *i.e.* in mine workings (pollution "at the source").

Keywords Barium, Purification, Sulphates, Mine waters

Introduction

Mine waters with chemical composition ranging from fresh waters to brines occur naturally in the Carboniferous formations of the Upper Silesian Coal Basin (USCB). Majority of them exhibit high concentration of chlorides, sodium, potassium, calcium, magnesium, sulphates and micro-components, especially barium. Some of these components reach the highest concentration reported for the undergroundwaters in the world (Rózkowski *et al.* 2004; Pluta 2005). Among them barium is particularly harmful in the water environment. Its concentration in waters flowing into mines exceed more than thousand (1000) times the highest permissible limit determined for waste waters- mine waters pumping from mines in Poland (Pluta and Pałys 1999; Pluta 2005; Ordinance of the Minister of Environment 2006). Waters discharged from coal mines of the Upper Silesia in Poland containing barium cause contamination of mine pipes in mine workings (Fig. 1a), especially the environmentally important pipeline of the Olza Collector (Fig. 1b), of settling ponds, of surface waters and their sediments (*e.g.* Bo-

jakowska and Sokołowska 1998; Pluta 2005). Its causes technical problems, *e.g.* the pollution ("overgrown" of pumps, pipe, pipelines) of water transport systems. Therefore, purification of coal mine waters from barium is an important mining and ecological task in the Upper Silesia (Poland). This problem is particularly serious for coal mines situated in the south-western part of the USCB (Pluta and Pałys 1999; Pluta 2011).

The simplest, and the most effective method of removal of barium from waters is its precipitation in the form of practically insoluble deposits, mainly sulphate, according to the following reaction:



The sources of ion sulphate (VI) in mines are different sulphur compounds contained in the Upper Carboniferous strata or in covering deposits, as well as substances used in mining operations. The most important process of sulphates generation is the oxidation of sulphides. As the effect of dissolving, leaching and oxidation, sulphates infiltrate into mine waters.



Fig. 1 Boring pipe from coal mine (a: left) and of the pipeline of the Olza Collector (b: right)

Since the 1990s various attempts to develop simple and economically sound methods to reduce the impact of barium on the aquatic environment have been undertaken. Particular attention was drawn to the use of mining activities. This paper explains all the used processes that reduce barium in coal mine waters of the USCB.

Removing barium from mine waters by sulphate minerals

In the Upper Silesian Coal Basin sea sediments of the Miocene and the Triassic occur. Some of them contain evaporated sulphate minerals, especially containing calcium: gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and anhydrite (CaSO_4). Their dissolving enriches the mine waters with sulphates. Mine waters can also dissolve sulphate minerals contained in the Upper Carboniferous deposits. Gypsum, anhydrite occur in different lithostratigraphic series (Kuhl 1955). Besides them hydrated sulphate minerals: epsomite ($\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$), jarosite ($(\text{Na,K})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$), melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) in the form of crusts and powder aggregates, mainly in fracture zones exist in the Upper Carboniferous coal-bearing deposits.

Removing barium from mine waters by sulphite minerals

Sulphates can also penetrate into mine waters as a consequence of the oxidation processes of sulphide minerals, and organic matter con-

taining different sulphur organic components. The disulfides occur in the Upper Carboniferous deposits as pyrite and marcasite (FeS_2). Under certain circumstances these substances can become the source of sulphates for the mine waters in contact with the coal-bearing strata. Sometimes this process is observed in water flowing through cavities made by extraction, gobs, old mine workings. This process was noticed for the first time in the "Silesia" coal mine (Pluta *et al.* 1994) and later in other coal mines in the south-western part of Upper Silesian Coal Basin (Pluta 2004).

Removing of barium by mine activities in mine workings

It is much preferred to carry out the mine waters treatment "at source" (reduction "at source"). Therefore, the substance causing mine waters contamination, especially barium, should be reduced or removed in the underground mine workings, *i.e.* at the point of origin of contamination rather than on the surface. The special chemical or biological methods of mine waters treatment are difficult, and above all expensive. The best method is the initiation of these processes in places where natural mine waters enter mine workings, removing of harmful substances *in situ* in the water-bearing layer or limitation of their amount during flow through a "protective barrier", "purifying barrier". Since 1990s attention was drawn to the possibility of purify mine wa-

ters from barium by means of the mining methods and technologies applied in mine workings.

The process of coal extraction is regulated by various laws and legal regulations particularly in the area of mine safety. Therefore, it is necessary to carry out many operations, among them such as: filling of underground cavities caused by the extraction, performance of roadside packs, construction of water and stopping gas dams. In these works different substances are used. Some of them contain sulphates and sulphides which can cause precipitation, oxidation or sorption of barium comprised in natural mine waters.

As it is mentioned above, barium can be removed from waters by its precipitation with of sulphates derived from sulphate minerals (products) – gypsum and anhydrite. These substances are used in some mining technologies. Gypsum and anhydrite are used in coal mines as an sealing mixture for fire protection. Anhydrite is also used for the protection of mine working places against overpressure of the Carboniferous rocks. These technologies were used in the "Morcinek" and "Jastrzębie" mines (Pluta and Ślaski 1993; Pluta 2001a).

Since the mid-1980s, the fine-grained industrial wastes have been utilized in coal mines. They have been used in different mining technologies, among others for self-consolidating filling, for filling (sealing) of longwalls and roadways, for performing of plugs and dams as well as roadside packs. Wastes from power plants contain mainly fly ashes and the flue gas desulphurisation products. These wastes contain sulphates: anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as well as hannabachite ($\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$). From these wastes in underground mine workings sulphates penetrate into mine waters. Systematic investigations of sulphates in the mine waters draining off from storage of wastes, have shown that their concentrations can reach 4150 mg/dm^3 . Their amounts depend on the mining technologies, type of wastes, type of coal used for combustion and the hydrogeological condi-

tions in the mine workings (Pluta *et al.* 2002, 2006; Pluta 2011).

The post-extraction cavities, gobs and old mine workings also are filled also with mining wastes. The wastes are mainly Carboniferous barren rocks, separated from the extracted coal in coal cleaning preparation. In these processes the fine-grained wastes derived from flotation and washing processes, as well as sediments from drainage roads are used. In these wastes, as in wastes from power plants sulphates occur. They originate from the oxidation processes of sulphur minerals contained in the Upper Carboniferous coal-bearing deposits. Generally their amounts are lower than in the case of the described above wastes originating in power plants. For example into the water of the "Borynia" mine about 500 mg of sulphates are released into 1 dm^3 of mine water from the flotation tailings. Sulphates contained in waters leaching from the places of power and mining wastes using in different technologies cause precipitation of barium from natural mine waters flowing into mine workings. These favourable effect of the reduction of the barium content in mine waters were observed for example during the storage of fly ashes in the "Pniówek" coal mine (Pluta and Waleczek 1996). Such a situation takes place in coal mines of the south-western part of the USCB where the natural mine waters contain barium. In the "Borynia" coal mine the technologies of placing of wastes have been optimized in order to maximize quantities of sulphates needed to be released into natural mine waters containing barium (Pluta and Piotrowski 2002).

Removing barium by sodium sulphate

Since the beginning of the XXI century natural processes of dissolution of sulphate minerals and desulphurisation products of the Carboniferous rocks and mining activities with industrial wastes rich in sulphur, as described above, were not enough to reduce the whole amount of barium present in natural mine wa-



Fig. 2 Feeders of sodium sulphate: in mine working (left) and on the surface (right)

ters. Therefore, since that time sodium sulphate (VI) has been used to purify saline waters from barium (Pluta 2001b). This substance is added into mine water in special feeders built in mine workings, sometimes also on the surface (Fig. 2). About three thousand tons of sodium sulphate are dissolved in mine water each year. This process results in removing barium from mine waters and at the same time keeps the water transportation systems free of this harmful component.

Summary and conclusions

Natural mine waters containing barium flow into mine workings of the Upper Silesian Coal Basin and the rivers of the Upper Silesia in Poland. This element cause contamination of mine workings, mine waters transportation systems, surface waters and their sediments, and its concentration in mine waters flowing from coal mines exceed the maximum permissible value in Polish Water Law (Ordinance of Minister of Environment 2006). Therefore, the content of barium should be reduced. For its removal or substantial decrease sulphates (VI) can be used. In coal mines of the Upper Silesia in Poland the natural processes, mining methods and technologies can be used. Sulphates (VI) ions can be obtained from waters with either the evaporated minerals or oxidation products of various sulphur compounds occurring in Carboniferous formation. Sources

of sulphates include: gypsum, anhydrite and industrial wastes such as: fly ashes, slags and flotation tailings. Gypsum and anhydrite are used in coal mine workings as components of an isolating mixture for fire protection. Anhydrite is also used for the protection of the wall of work places against overpressure. Industrial wastes: fly ash, slags from electric plants and flotation tailings from coal mines are stored in the mine workings, especially in gobs as fire and methane protection agents. Development of clean-burning-coal technologies produces wastes with high concentration of sulphur. Since the beginning of the XXI century the purification of mine waters by sodium sulphate has been used.

Majority of the methods described above are examples of the most favorable reduction of pollution "at the source" of its arising, *i.e.* underground, and they do not need any capital outlays.

Use of mining methods and technologies and application of wastes from the power and coal mines in purification of mine waters is unique on the world scale, therefore the project was awarded at the IMWA international congress held in Sevilla in 1999.

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