

---

## An attempt towards the safe utilisation of dangerous sediments deriving from mine water: a case study from the Polish part of the Upper Silesian Basin

---

Bogusław Michalik\*, Hubert Makuła and  
Zbigniew Bzowski

Central Mining Institute (GIG),  
40-166 Katowice, Plac Gwarków 1, Poland

Email: [bmichalik@gig.eu](mailto:bmichalik@gig.eu)

Email: [hmakula@gig.eu](mailto:hmakula@gig.eu)

Email: [zbzowski@gig.eu](mailto:zbzowski@gig.eu)

\*Corresponding author

**Abstract:** The removal of formation waters from coal mines in the Upper Silesian Basin is the source of sediments. Due to high content of radium, the sediments are classified as naturally occurring radioactive materials (NORMs) and require special treatment according to the current EU and IAEA recommendations. On the other hand, the sediments contain potentially marketable materials and elements when separated. With this in mind, the radiometric, mineralogical, and physicochemical studies were conducted to characterise the sediments from the perspective of possible reprocessing. In the sediments high content of baryte was found, which is an interesting feature, since baryte is included in the list of critical raw materials (CRMs) crucial to the European economy. As a mineral, baryte can precipitate from underground waters or originate from gangues and it frequently contains radium. The research provides valuable information concerning the concentration and the forms of baryte present in the examined sediments. In particular, the concentration of radium as well as the purification process of the remaining sediments with potential applications in construction is discussed.

**Keywords:** mine water; sediments; naturally occurring radioactive material; NORM; minerals; barite; radium; recovery.

**Reference** to this paper should be made as follows: Michalik, B., Makuła, H. and Bzowski, Z. (2022) 'An attempt towards the safe utilisation of dangerous sediments deriving from mine water: a case study from the Polish part of the Upper Silesian Basin', *Int. J. Mining and Mineral Engineering*, Vol. 13, No. 1, pp.49–63.

**Biographical notes:** Bogusław Michalik graduated from the Silesian University in 1982 majoring in Applied Physics, and received his PhD in Environmental Engineering from Central Mining Institute, Katowice, Poland in 2002, and then DSc in Habilitation in 2012. Currently, he has position of an Associate Professor in the Central Mining Institute, Poland. His research interests include the theory and practice of radiation protection and radioecology especially focused on environmental radioactivity and naturally occurring radioactive materials.

Hubert Makuła is a geologist and started his professional carrier in the Department of Environmental Monitoring, Central Mining Institute. He is involved in waste landfill monitoring, sampling and waste reprocessing. Currently, he is preparing background to his possible PhD thesis aimed at recycling of mine sediments.

Zbigniew Bzowski is a geologist and has specialised in mineralogy and waste classification and recycling with more than 30 years' experience in XRF application and mineralogical data analysis. Currently, he is working in the Department of Environmental Monitoring, Central Mining Institute, responsible for waste landfill monitoring, sampling and ERA procedures.

This paper is a revised and expanded version of a paper entitled 'Barite in sediments from underground waters of hard coal mines of the Upper Silesian Coal Basin (Poland)' presented at 28th International Symposium on Mine Planning and Equipment Selection – MPES 2019, Pan Pacific Perth, Perth, Australia, 2–4 December 2019.

---

## 1 Introduction

Bituminous coal mining in the Upper Silesian Basin (southern Poland), which still is the pillar of the Polish economy, dates back to the mid-19th century. The necessary action aimed at providing access to bituminous coal seams and ensuring the safety of miners is to remove mine water from underground excavations to natural surface watercourses. Carboniferous sediments subjected to epigenetic processes are a source of radium isotopes for groundwater circulating in them. Underground water in the Upper Silesian Basin, in addition to radium isotopes, is also a carrier of suspension and many other chemical compounds that can negatively affect the composition of surface waters.

Accumulation of underground water in settling tanks results in the sedimentation and crystallisation processes, which lead to the separation of the aforementioned compounds. While adapted and closed underground excavations can be used as underground water sedimentation tanks, natural water reservoirs or artificial ponds can be used above the ground.

Discharge of the underground waters to the settlers is associated with the formation of sediments, which frequently contain valuable chemical compounds due to the possibility of their subsequent use. This includes barium sulphate (baryte) but due to presence of radium dissolved in underground waters, baryte often occurs as radium-barium sulphates (Chałupnik and Wysocka, 2008; Michalik, 2011; Leopold et al., 2013; Chałupnik et al., 2017; Jirásek et al., 2020). In general, in radium rich formation waters,  $Ra^{2+}$  ions may coprecipitate with other cations present, usually as insoluble sulphates such as  $BaSO_4$ ,  $SrSO_4$  or  $CaSO_4$ . Usually, in coal mines radium coprecipitates with barium  $Ba^{2+}$ . During the nucleation phase the most abundant barium ions can be replaced by radium (as well as Sr, Pb) ions (Ceccarello et al., 2004). Finally, the process may result in complex sulphates, e.g.,  $Ba(Ra, Sr)SO_4$ . However, depending on the chemical composition of specific formation water,  $Ra^{2+}$  may coprecipitate also with calcium carbonate (Zielinski et al., 2001). The possibility of precipitation of baryte from solutions with an increased content of Ba, Pb, Sr and Ra ions is quite well known (e.g., Brandt et al., 2015; Vinograd et al., 2018) and commonly applied in radiochemistry for the radium extraction from

solutions. Presence of  $\text{Ra}^{2+}$  ions in carbonates has been described by Matyskin et al. (2017). However, the current state of knowledge does not allow for the determination of the efficiency of the precipitation process of radium sulphates or carbonates from the formation water as a radium carrier. One can only presume that this process leads to the creation of a source of much greater concentration of radium isotopes than the average amounts found in the Earth crust (UNSCEAR, 2000). Moreover, there are several issues present, regarding also the occurrence of strontium and lead substitutions in the barytes present in the sediments. Therefore, the main aim of the conducted research is to assess the concentration of baryte and its forms present in the sediments. Besides baryte, the mineral and chemical composition of the sediments corresponds mainly to sandstones – the most common residue of Upper Carboniferous rocks in the Upper Silesian Basin. The mineralogical studies of the sediments carried out so far have also led to the identification of carbonates, iron oxyhydroxides and other than baryte sulphates, crystallising from underground waters (Bzowski and Michalik, 2015). That is why, when examining the forms of baryte, one should analyse not only whether baryte, which is a radium carrier in the studied sediments, may serve as a source of radium but also if purified baryte, as well as emerged residues are suitable for utilisation.

Apart from coal mining, similar processes resulting in radium-rich sediments or scales are observed frequently in non-ferrous metal ore mining and particularly in oil and natural gas extraction (IAEA, 2003).

Currently, all the sediments precipitating from the underground waters pose significant technical and environmental challenges, particularly due to the high radium content (Michalik, 2011; Wysocka et al., 2019). On the other hand, this offers the worthwhile possibility of their utilisation as a source of pure radium and radium-free baryte.

## **2 Material and methods**

The research material consists of 22 samples taken from two coal mines located in the southern part of the Upper Silesian Basin (Figure 1). The samples are used to analyse the volume of heavy metals and mineral composition found in sediments. The selected coal mines discharge formation waters varying significantly in their chemical composition, particularly when the barium content is considered. Laboratory samples of the sediment were selected from averaged samples collected routinely in the course of the monitoring activities regarding radiation risk in underground coal mines.

Thanks to the gamma spectrometer, equipped with high purity germanium detector (HPGe), reaching a detection limit below 1 Bq/kg with high resolution, the survey of the activity concentration was carried out directly for each of the radionuclides and the given expanded uncertainty was confirmed with the 1-sigma significance in accordance with the certified internal procedure of the Silesian Centre for Environmental Radioactivity (Central Mining Institute). In the samples tested, significant concentrations of the natural decay series parent radionuclides such as  $^{238}\text{U}$  or  $^{232}\text{Th}$  were absent, while both relevant radium isotopes, i.e.,  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ , were abundant.  $^{226}\text{Ra}$  was measured directly at energy photo peak 186 keV. Additionally, after equilibrium had been reached,  $^{226}\text{Ra}$  decay products,  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$ , were measured at the following gamma energy photo peaks: (295 and 351 keV) and (609 keV), respectively.  $^{228}\text{Ra}$  activity concentration was

evaluated based on the direct measurement of  $^{228}\text{Ac}$  at 911 keV photo peak.  $^{228}\text{Th}$  and  $^{224}\text{Ra}$ , under the well-justified assumption of being in secular equilibrium in the samples, were measured by their decay products as  $^{212}\text{Pb}$  (at 238 keV) and  $^{208}\text{Tl}$  (at 583 keV) corrected for the decay type ratio. The samples were dried in an oven at  $105^\circ\text{C}$  for stable mass, then they were sieved through a 2 mm sieve and the test samples were packed into Marinelli containers. All activity concentrations were calculated for sediments dry mass.

**Figure 1** Localisation of the Chwałowice and Jankowice coal mines in the Upper Silesian Basin (Poland); made by authors (see online version for colours)



Chemical studies on the content of trace elements, including heavy metals, were carried out by X-ray dispersion spectrometry (XRF). The determinations were performed in accordance with the accredited procedures of the Solid Waste Analysis Laboratory (Central Mining Institute) using XRF Primus 2 from Rigaku Corporation.

The research of the mineral composition was conducted using powder (DSH) diffractometric method in Bragg-Brentano geometry and LYNXEYE\_XE detector, Ni filter and  $\text{CuK}\alpha$  radiation. D8 Discover diffractometer by Bruker was used at the Department of Environmental Monitoring (Central Mining Institute) for testing and DIFFRAC v.4.2 and TOPAS v.4.2 (Bruker software) programs for registration and diagnostics. The qualitative mineral composition was established by means of the standards licensed in the International Centre for Diffraction Data (ICDD) database under the names PDF-4+ 2020 and PDF-4+ 2021 as well as in the databases: NIST and ICSD.  $\text{ZnO}$  was used as an internal standard to carry out quantitative studies of the mineral composition.

Quantitative calculations of the crystalline phases and amorphous substance were made basing on the Rietveld methodology (Rietveld, 1969; Rodriguez-Carvajal, 1997; Mahieux et al., 2010; Bortolotti et al., 2017).

**Table 1** The content of  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ ,  $^{228}\text{Th}$  ( $^{224}\text{Ra}$ ),  $^{40}\text{K}$  and activity concentration index (I) in the examined sediments

Sample no.	$^{226}\text{Ra}$	$^{228}\text{Ra}$	$^{228}\text{Th}$ ( $^{224}\text{Ra}$ )*	$^{40}\text{K}$	I
	kBq/kg			Dimensionless	
10/19	68.0	18.4	16.5	0.5	319
9/19	65.9	14.9	15.6	0.7	294
8/19	49.1	25.2	17.1	0.4	290
36/19	40.1	20.0	8.6	0.3	234
35/19	40.0	20.0	9.1	0.5	233
38/19	29.0	15.3	6.9	0.5	173
19/19	29.0	15.3	6.9	1.1	174
7/19	28.1	12.5	2.9	1.7	157
6/19	27.0	11.2	3.3	1.2	146
37/19	25.9	13.4	6.0	1.0	154
5/19	22.9	10.6	3.9	0.2	129
4/19	18.6	5.8	2.8	0.3	91
23/19	18.6	1.5	2.1	0.2	69
21/19	15.4	8.9	2.1	0.5	96
3/19	13.7	3.8	3.1	1.5	65
34/19	12.0	3.5	1.5	1.0	58
2/19	11.5	5.0	1.3	1.1	64
22/19	11.3	0.9	1.1	1.2	42
33/19	11.0	0.8	1.1	1.2	41
32/19	4.9	0.8	0.7	0.5	21
1/19	2.7	0.8	0.3	0.5	13
31/19	1.9	1.1	0.2	0.4	12

Note: \* $^{228}\text{Th}$  and  $^{224}\text{Ra}$  under real conditions these radionuclides are in secular equilibrium state.

### 3 Research results

#### 3.1 Activity concentration of radium isotopes

Activity concentration of radium isotopes  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  varies in the tested samples of the sediment in the range 1.9–68 kBq/kg and 1.1–18.4 kBq/kg respectively (Table 1). Additionally, activity concentration of  $^{228}\text{Th}$  and  $^{224}\text{Ra}$  that are in secular equilibrium reaches 16.5 kBq/kg and in some cases is greater than activity concentration of  $^{228}\text{Th}$ , which indicates that the tested sediments are more than five years old. According to the existing European regulations in radiation protection (Council Directive, 2013) none of

the sediment samples meet clearance level for  $^{226}\text{Ra}$  as well as for  $^{228}\text{Ra}$  and therefore sampled sediments require a special treatment. Furthermore, the sediments in question are not suitable for a utilisation in construction as indicated by the activity concentration index (I) calculated on the basis of radium, thorium and potassium activity concentration (I in building materials should be  $< 1$ ) (Table 1). Assuming that radium isotopes are enclosed in baryte, which constitutes a few percent of the total mass of the sediments, one should expect the activity concentration in pure baryte to be significantly greater. This makes baryte extracted from the sediment unusable in construction and any other direct prospective applications.

### 3.2 *Metal content in the tested sediments*

The results of the examination of metals such as barium, strontium, lead, manganese, copper, chromium, and zinc present in the underground water sedimentation tanks in two bituminous coal mines subject to investigation (Table 2) indicate that their concentrations are associated with various mineral phases.

**Table 2** The content of barium, strontium, lead, manganese, copper, chromium and zinc in the examined sediments

<i>Sample no.</i>	<i>Ba</i>	<i>Sr</i>	<i>Mn</i>	<i>Cu</i>	<i>Cr</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
	%							
1/19	0.88	0.04	330	50	68	46	70	132
2/19	10.48	0.65	210	90	97	77	120	126
3/19	11.90	1.29	2,360	< 10	< 10	69	< 10	190
4/19	10.92	1.20	1,580	73	106	61	60	186
5/19	8.37	0.12	668	56	94	63	< 10	123
6/19	12.72	1.16	1,350	80	< 10	180	< 10	243
7/19	21.13	3.82	380	100	130	107	120	166
8/19	36.26	3.32	820	< 10	< 10	90	105	190
9/19	39.49	3.50	400	< 10	< 10	< 10	230	84
10/19	44.10	4.18	530	< 10	< 10	94	750	72
19/19	30.50	3.20	230	44	< 10	< 10	135	280
21/19	13.20	1.42	1,650	< 10	142	78	< 10	242
22/19	13.70	1.49	1,690	< 10	112	95	< 10	179
23/19	18.50	1.71	1,110	< 10	< 10	74	< 10	213
31/19	0.90	0.05	460	210	120	55	< 10	344
32/19	2.33	1.02	800	< 10	55	53	80	1,080
33/19	8.77	1.30	420	38	77	41	< 10	500
34/19	11.73	1.44	340	55	65	80	< 10	380
35/19	39.10	3.28	52	< 10	< 10	70	115	430
36/19	40.74	3.63	88	38	< 10	60	180	140
37/19	36.60	4.30	72	49	30	100	285	185
38/19	36.86	6.50	630	56	< 10	88	400	220

### 3.3 Mineral composition of the sediments

Table 3 presents the results of the analyses of the crystalline phases present in the tested samples of the sediments created from the underground waters released from two investigated mines. In the mineral composition the presence of amorphous substance containing bituminous coal was identified. Mineral phases of the studied sediments originate mostly from rocks surrounding coal seams. However, they are noticeably supplemented by minerals precipitating in the sedimentation tanks and anthropogenic minerals supplied as the result of mining activities.

**Table 3** Results of analyses of the crystalline phases present in the tested sediments

<i>Minerals associated with coal scales present in the sediments from the sedimentation tanks</i>
Quartz $\text{SiO}_2$
K-feldspars $\text{K}[\text{AlSi}_3\text{O}_8]$
Hematite $\alpha\text{-Fe}_2\text{O}_3$ , goethite $\alpha\text{-FeO(OH)}$ , pyrite $\text{FeS}_2$
Sulphates: baryte $\text{BaSO}_4$ , jarosite $\text{KFe}_3(\text{SO}_4)(\text{OH})_6$ , gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Carbonate minerals: calcite $\text{CaCO}_3$ , siderite $\text{FeCO}_3$ , dolomite $\text{CaMg}(\text{CO}_3)_2$ , ankerite $\text{Ca}(\text{Fe}, \text{Mg})(\text{CO}_3)_2$
Clay minerals: illite $(\text{K}, \text{H}_3\text{O}^+)\text{Al}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$ , chlorite $(\text{Mg}_5\text{Al})[\text{AlSi}_3\text{O}_{10}](\text{OH})_8$
Montmorillonite $\text{Ca}_{0.2}(\text{Al}, \text{Mg})_2[(\text{OH})_2\text{Si}_4\text{O}_{10}] \cdot 4\text{H}_2\text{O}$ , kaolinite $\text{Al}_4[\text{Si}_4\text{O}_{10}](\text{OH})_8$ , biotite $\text{K}(\text{Mg}, \text{Fe}, \text{Mn})_3[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$ , muscovite $\text{KAl}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2$
<i>The precipitated minerals in the sedimentation tanks</i>
Halite $\text{NaCl}$
Sulphates: baryte $\text{BaSO}_4$ , jarosite $\text{KFe}_3(\text{SO}_4)(\text{OH})_6$ , gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Calcite $\text{CaCO}_3$
Hematite $\alpha\text{-Fe}_2\text{O}_3$ , goethite $\alpha\text{-FeO(OH)}$
<i>The anthropogenic minerals in the sedimentation tanks</i>
Magnetite $\text{FeFe}_2\text{O}_4$ , hematite $\alpha\text{-Fe}_2\text{O}_3$
Mullite $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$

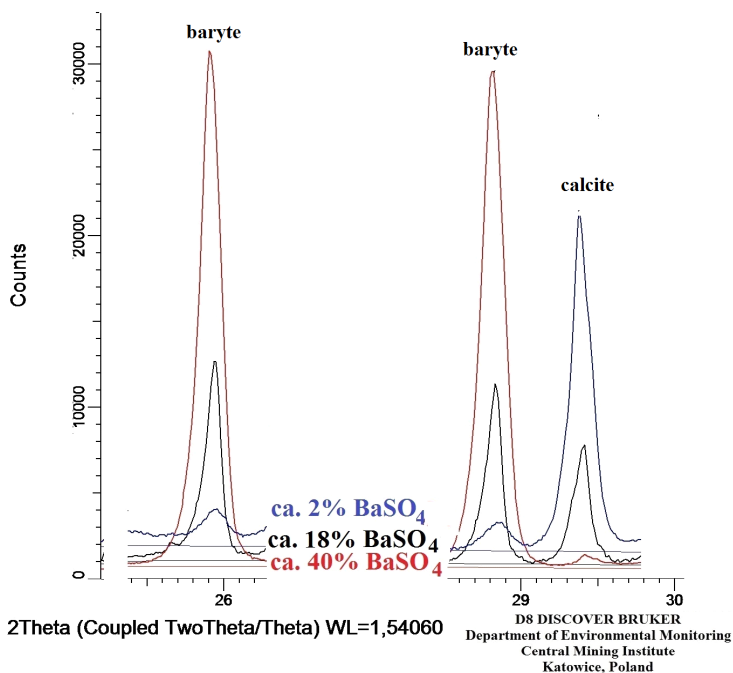
Note: Chemical formulas according to Bolewski and Manecki (1993)

It is worth noticing that the most abundant minerals in the sediment samples were quartz, baryte, calcite and clay minerals. These minerals are usually accompanied by feldspar, both potassium microcline or orthoclase, and sodium albite. In the studied sediments, apart from baryte, other sulphates were found, such as gypsum and jarosite (Matýsek et al., 2014), carbonates in the association with dolomite – ankerite – siderite and sulphides, iron oxides and hydroxides. Anthropogenic minerals such as magnetite, hematite and mullite present in the investigated sediments are associated with materials used for fire prevention of underground excavations (Plewa and Mysłək, 2001; Plewa et al., 2013; Drobek et al., 2016; Proksa et al., 2020). The mineral phases washed out from these materials are transported by groundwater and deposited in the sedimentation tanks (Bzowski and Michalik, 2015).

In the studied sediments baryte is present in concentrations ranging from about 2% to over 40%. The concentrations of baryte in these sediments have been documented by the mineralogical research (Figure 2) and chemically confirmed by the determination of

barium content (Table 2). Examples of the diffraction patterns of the sediment samples with varying baryte content are presented in Figure 2.

**Figure 2** Examples of the diffraction patterns of the sediment samples with varying baryte content (see online version for colours)



### 3.4 Discussion – baryte forms

Baryte ( $\text{BaSO}_4$ ) crystallises in the rhombic bipyramid class (Pnma), similarly to strontium sulphate – celestine ( $\text{SrSO}_4$ ), lead sulphate – anglesite ( $\text{PbSO}_4$ ) and radium sulphate ( $\text{RaSO}_4$ ). In the examined sediments baryte can originate from two sources. The first source is productive carboniferous coal: a rock in which baryte is present as an accessory or epigenetic mineral in hydrothermally mineralised fissures crossing sedimentary formations. This form of baryte appears in the sediments under investigation as a result of mining works related to bituminous coal exploitation. The second source of baryte is a result of precipitation and crystallisation of  $\text{BaSO}_4$  substances from  $\text{Ba}^{2+}$  and  $\text{SO}_4^{2-}$  ions present in underground waters and discharged into the sedimentation tanks (Curti et al., 2010; Grandia et al., 2008; Torapava et al., 2014). The barium supplied to the water is present in bituminous coal, and sulphates are formed as a result of oxidation of iron sulphides found in both bituminous coal and coal rocks.

The baryte forms found in the sediments are directly related to the sources of supply or formation of this mineral in the sediment. X-ray diffraction (XRD) proved that the basic form of the baryte is almost ‘pure’  $\text{BaSO}_4$  crystalline phase without admixtures of other ions in place of barium (Figure 3). It is probably the baryte originating from the Upper Carboniferous sediments and rapidly precipitated in underground waters flowing directly from the exploited bituminous coal walls. The sediment with baryte in this form



contains less than 10 mg Pb/kg and not more than 500 mg Sr/kg. The second form of baryte takes the phase form of the crystalline compound BaSO<sub>4</sub> containing strontium and occurs alongside the first form (Figure 3).

**Figure 3** Fragments of diffraction patterns documenting three phases of baryte in the studied sediments

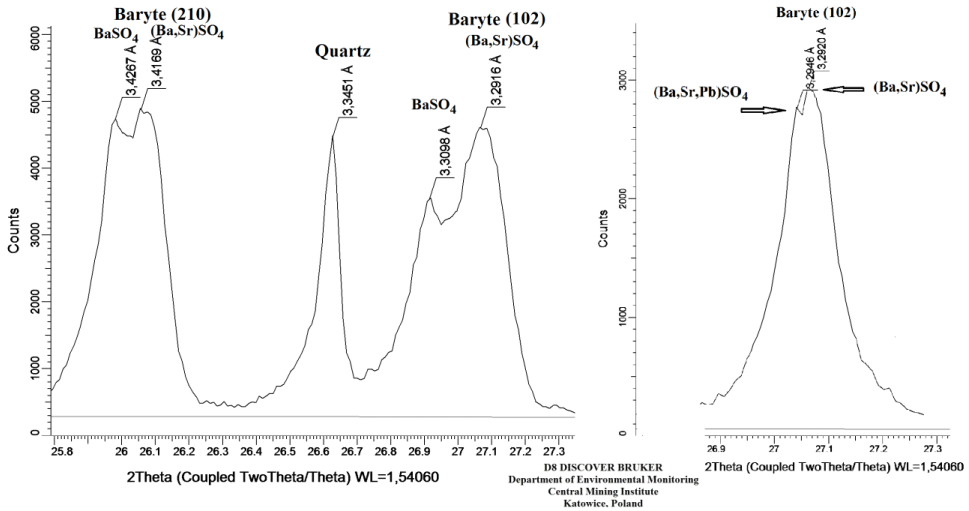


Table 4 presents the XRD diagnostic data for these three forms of baryte. Based on the data (PDF-4+ 2019 ICDD database), the relationship between the amount of strontium in baryte and the *d* lattice values for the indicated *hkl* faces was determined (Figure 4).

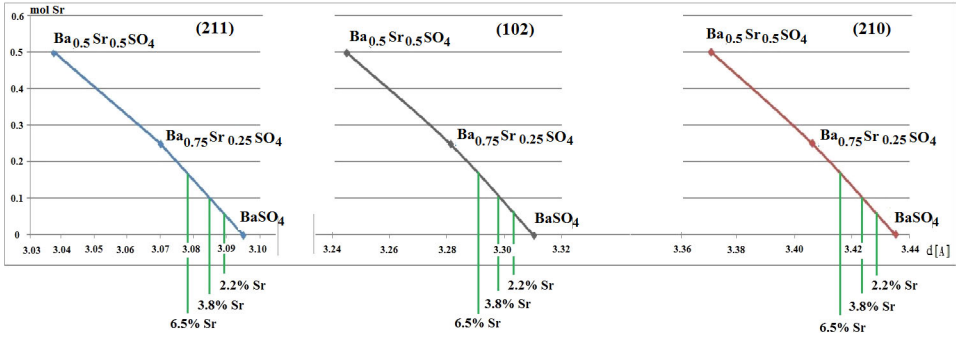
**Table 4** Diagnostic data (PDF-4+ 2019 ICDD database) for forms determined by the XRD method

<i>hkl</i>	BaSO <sub>4</sub>	Ba <sub>0.8</sub> Pb <sub>0.2</sub> SO <sub>4</sub>	Ba <sub>0.69</sub> Pb <sub>0.31</sub> SO <sub>4</sub>	PbSO <sub>4</sub>
	<i>d</i> values (Å)			
210	3.435	3.417	3.413	3.333
102	3.310	3.296	3.287	3.215
211	3.095	3.080	3.075	3.012
<i>hkl</i>	BaSO <sub>4</sub>	Ba <sub>0.75</sub> Sr <sub>0.25</sub> SO <sub>4</sub>	Ba <sub>0.5</sub> Sr <sub>0.5</sub> SO <sub>4</sub>	SrSO <sub>4</sub>
	<i>d</i> values (Å)			
210	3.435	3.406	3.371	3.300
102	3.310	3.281	3.245	3.175
211	3.095	3.070	3.038	2.978

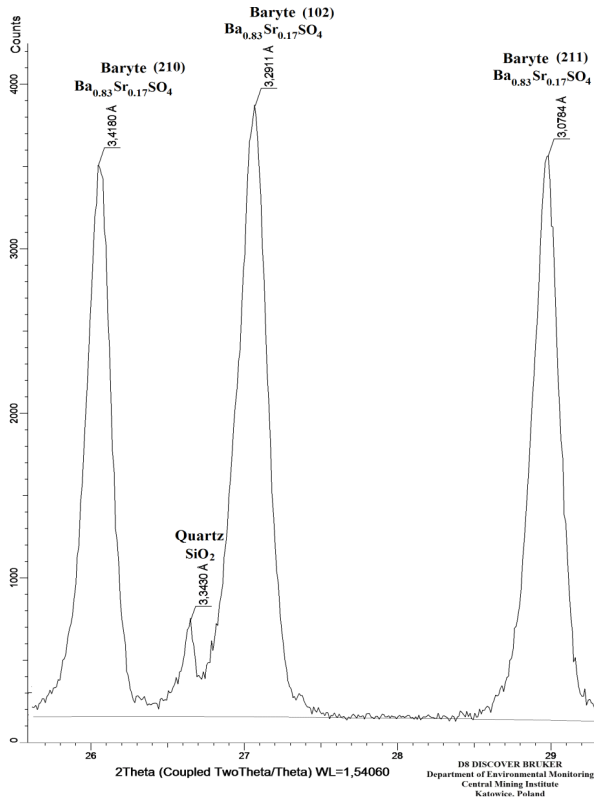
The charts (Figure 4) show the sediment samples in which the strontium content was maximal – 6.5%, frequently encountered – 3.8% and average – 2.2%. Because a significant correlation between barium and strontium concentrations was found in the studied sediments, with the value of 0.88 at the significance level  $\alpha = 0.005$  for  $n = 22$ , it can be assumed that all of the strontium present is bound in baryte. Thus, the baryte form with strontium present is expressed by the formula Ba<sub>0.83</sub>Sr<sub>0.17</sub>SO<sub>4</sub> corresponding to the

concentration of 6.5% of strontium,  $Ba_{0.90}Sr_{0.10}SO_4$  for 3.8% Sr and  $Ba_{0.94}Sr_{0.06}SO_4$  for the average content of 2.2% Sr.

**Figure 4** Relations between concentration of strontium in baryte and  $d$  lattice values for indicated  $hkl$  faces as well as such relations in strontium barytes of the examined sediments (see online version for colours)



**Figure 5** A fragment of the diffraction pattern of the sample containing 6.5% Sr (barium concentrate)



Using the data from the XRD (ICDD, 2021) database for strontium barytes containing 0.25 and 0.5 moles of strontium it has been determined that the specific gravity of baryte

forms  $Ba_{0.75}Sr_{0.17}SO_4$  and  $Ba_{0.94}Sr_{0.06}SO_4$  are equal  $4.40 \text{ g/cm}^3$  and  $4.45 \text{ g/cm}^3$  respectively. Those values are close to the value of specific gravity of the ‘pure’ baryte, which is equal to  $4.5 \text{ g/cm}^3$ .

Therefore the method of flotation, based on relative densities of the constituents, cannot be used as a separation method of the baryte forms in the sediment.

Lattice values  $d$  for 210, 102 and 211 strontium baryte faces in the examined sediments with the given molar relations (Figure 4) were found from the diffraction patterns (Figure 5).

The third form of baryte is the crystalline compound  $BaSO_4$  containing strontium and lead, the presence of which was confirmed in only a single sample of the studied sediments by the detailed XRD analysis (Figure 3). In this sample 4.18% Sr was found, which, assuming the entirety of strontium in baryte, constitutes 0.11 mole of Sr ( $Ba_{0.89}Sr_{0.11}SO_4$ ) and 750 mg Pb/kg. Most probably only some part of lead is associated with baryte because the correlation coefficient between Ba and Pb content in the studied sediments ( $n = 22$ ) equals 0.70 at the significance level  $\alpha = 0.005$ . Therefore, the presence of lead in the studied baryte does not exceed 0.01 mole, and the baryte formula can be written as  $Ba_{0.88}Sr_{0.11}Pb_{0.01}SO_4$ . Despite precise measurements with extended registration times, identification of such a phase is exceedingly difficult, because there is no appropriate strontium-lead standard in the XRD PDF-4+ 2019 ICDD database. The only available standard in this database: lead-strontium baryte  $Ba_{0.977}Pb_{0.013}Sr_{0.01}SO_4$  does not match the diffraction patterns of the tested sediment samples.

The analysis of the presented mineralogical results of the sediments from the underground and surface sedimentation tanks of groundwater from bituminous coal mines of the Upper Silesian Basin confirmed the presence of various forms of baryte. However, due to the lack of precise diffraction pattern standards, it is difficult to implement the XRD method to identify radium baryte (Ba, Ra) $SO_4$ , synthesised and described (Brandt et al., 2015) and strontium-radium baryte (Ba, Sr, Ra) $SO_4$  (Vinograd et al., 2018). Most probably, both forms of baryte are present in the studied sediments due to the significant correlations between the concentration of barium, strontium, lead, and radium isotopes (Table 5).

**Table 5** Correlations between concentrations of Ba, Sr, Pb and  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$  in the studied sediments at the significance level  $\alpha = 0.005$

$N = 22$	<i>Ba</i>	<i>Sr</i>	<i>Pb</i>
$^{226}\text{Ra}$	0.87	0.67	0.68
$^{228}\text{Ra}$	0.83	0.68	0.48

No correlations were found between the contents of barium and strontium and the amounts of manganese, copper, chromium, and zinc (Bzowski and Michalik, 2015). The calculated correlation coefficients are generally negative (Table 6). Results of mineralogical tests suggested Ba, Sr and Pb are bound in sulphates, therefore this entails that the remaining metals should be associated with coexistence of sulphides and aluminosilicates or are not associated with mineral phases and subject to sorption on clay minerals, iron compounds or organic substance. Considering the noticeable correlation between radium and barium, this confirms previous suggestions that sorption of radium by clay minerals is limited (Michalik, 2011). This observation is important since extraction of the mineral phases containing radium, sulphates and carbonates from the

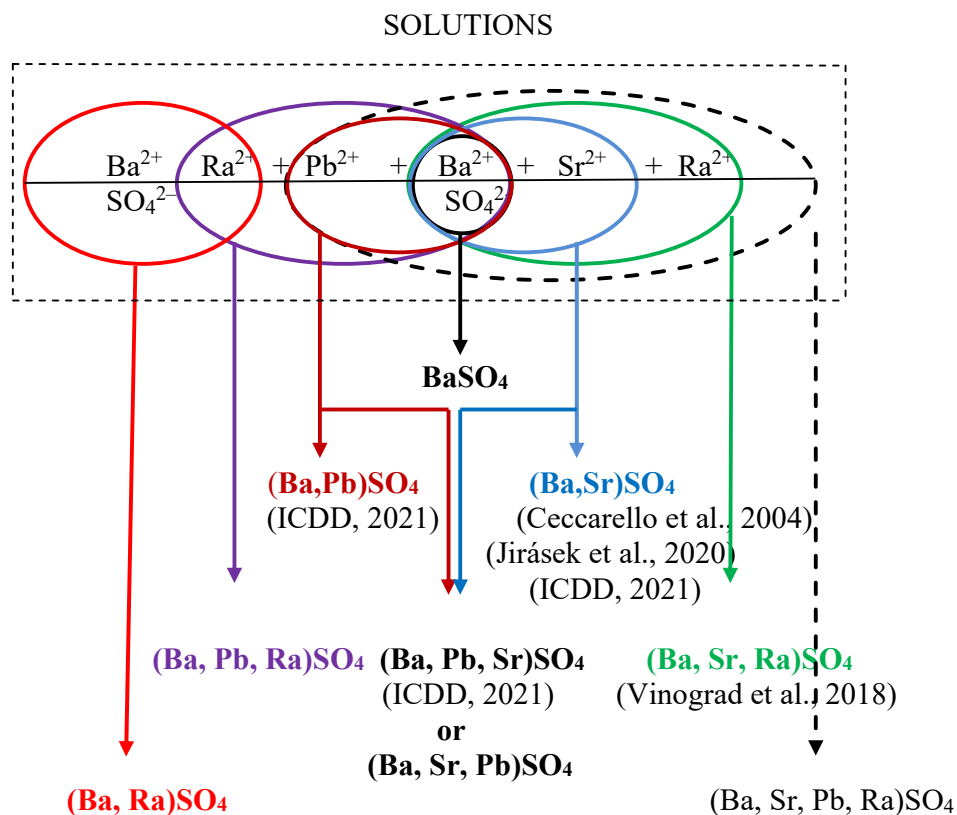
sediments would leave the remaining sediment free of radioactive contamination with possible use in construction industry.

**Table 6** Correlations between concentrations of Cr, Cu, Mn, Ni and Zn in the studied Ba and Sr sediments at the significance level  $\alpha = 0.005$

$N = 22$	<i>Cr</i>	<i>Cu</i>	<i>Mn</i>	<i>Ni</i>	<i>Zn</i>
Ba	-0.65	-0.38	-0.19	-0.02	0.04
Sr	-0.52	-0.26	-0.20	0.07	0.14

Keeping in the mind all the results, one can compose the general picture of the presence of baryte forms in the examined sediments from the water sedimentation tanks of Upper Silesian Basin (Figure 6).

**Figure 6** The baryte forms in the examined sediments – the proposed scheme (see online version for colours)



#### 4 Summary

The identified forms of baryte present in the sediments from the underground and surface sedimentation tanks of groundwater released from bituminous coal mines of the Upper

Silesian Basin (Poland) are 'pure' baryte with a trace content of strontium, i.e., strontium baryte and probably strontium-lead baryte. Correlations between concentrations of radium isotopes and the abundance of barium and strontium indicate connections between radium and barium in baryte, strontium baryte as well as strontium baryte with lead. While XRD shows barium and strontium diadochy in the baryte forms present in the studied sediments, it is difficult to capture radium diadochy due to very low abundance of radium isotopes, which, even in the case of the most active sediments, when expressed in mass units reaches merely a few ppm. Investigations into this issue can be conducted after the separation of baryte from the sediments, for example by flotation (Ren et al., 2017). In comparison to specific gravity of baryte equal to  $4.5 \text{ g/cm}^3$ , specific gravity of strontium baryte in the examined sediments lies in the range  $4.40\text{--}4.45 \text{ g/cm}^3$ . Therefore, due to small differences in specific gravity, flotation cannot be used as a method of the separation of various baryte forms in the sediments. Therefore, it must be assumed that there is no possibility to concentrate radium isotopes using this method. However, removal of all baryte forms, including radium, from the analysed sediments would lead to the clay-quartz material suitable for industrial utilisation free of radioactive contamination. The content of the amorphous phase in the sediments, after the elimination of baryte, has no impact on the prospects of their utilisation as a resource. Condensed baryte with relevantly high radium activity concentration can be used as a raw material for pure  $^{226}\text{Ra}$  production with potential applications in nuclear medicine. However, the problem of the separation of pure (radium free) baryte from the mixture of different baryte forms in the sediments is a subject of further investigations. The possibility of enrichment of the radium content remains a significant technological challenge.

## References

- Bolewski, A. and Manecki, A. (1993) *Mineralogy*, in Polish, Warsaw, Poland.
- Bortolotti, M., Lutterotti, L. and Pepponi, G. (2017) 'Combining XRD and XRF analysis in one Rietveld-like fitting', *Power Diffraction*, Vol. 32, No. S1, pp.S225–S230, DOI: 10.1017/S0885715617000276.
- Brandt, F., Curti, E., Klinkenberg, M., Rozov, K. and Bosbach, D. (2015) 'Replacement of baryte by a (Ba, Ra)SO<sub>4</sub> solid solution at close-to-equilibrium conditions', *Geochimica et Cosmochimica Acta*, No. 155, pp.1–15.
- Bzowski, Z. and Michalik, B. (2015) 'Mineral composition and heavy metal contamination of sediments originating from radium rich formation water', *Chemosphere*, March, Vol. 122, pp.79–87.
- Ceccarello, S., Black, S., Read, D. and Hodson, M.E. (2004) 'Industrial radioactive baryte scale: suppression of radium uptake by introduction of competing ions', *Minerals Engineering*, February, Vol. 17, No. 2, pp.323–330.
- Chałupnik, S. and Wysocka, M. (2008) 'Radium removal from mine waters in underground treatment installations', *Journal of Environmental Radioactivity*, October, Vol. 99, No. 10, pp.1548–1552.
- Chałupnik, S., Wysocka, M., Janson, E., Chmielewska, I. and Wiesner, M. (2017) 'Long term changes in the concentration of radium in discharge waters of coal mines and Upper Silesian rivers', *Journal of Environmental Radioactivity*, May, Vol. 171, pp.117–123.

- Council Directive (2013) *Council Directive 2013/59/Euratom of 5 December 2013 Laying Down Basic Safety Standards for Protection Against the Dangers Arising from Exposure to Ionising Radiation, and Repealing Directives 89/618/Euratom, 90/641/Euratom, 96/29/Euratom, 97/43/Euratom and 2003/122/Euratom*.
- Curti, E., Fujiwara, K., Iijima, K., Tits, J., Cuesta, C., Kitamura, A., Glaus, M.A. and Müller, W. (2010) 'Radium uptake during baryte recrystallization at  $23 \pm 2^\circ\text{C}$  as a function of solution composition: an experimental  $^{133}\text{Ba}$  and  $^{226}\text{Ra}$  tracer study', *Geochimica et Cosmochimica Acta*, 15 June, Vol. 74, No. 12, pp.3553–3570.
- Drobek, L., Kanafek, J. and Pierzyna, P. (2016) *Utilisation of CCPS in Hard-Coal Mines – Current State, Prospects for Years 2016–20, the Technical and Environmental Aspects*, in Polish [online] <http://unia-ups.pl/wp-content/uploads/2016/12/Drobek.pdf> (accessed 20 August 2020).
- Grandia, F., Merino, J. and Bruno, J. (2008) *Assessment of the Radium-Barium Co-Precipitation and its Potential Influence on the Solubility of Ra in the Near-Field*, SKB Technical Report, No. TR-08-07, SKB, Stockholm, Sweden.
- IAEA (2003) *Radiation Protection and the Management of Radioactive Waste in the Oil and Gas Industry*, Safety Reports Series, No. 34, International Atomic Energy Agency, Vienna.
- International Centre for Diffraction Data (ICDD) (2021) *International Centre for Diffraction Data PDF-4+*, USA.
- Jirásek, J., Matýšek, D., Alexa, P., Osovský, M., Uhlář, R. and Sivek, M. (2020) 'High specific activity of radium isotopes in baryte from the Czech part of the Upper Silesian Basin – an example of spontaneous mine water treatment', *Minerals*, Vol. 10, No. 103, pp.1–11 [online] <http://www.mdpi.com/journals/minerals>.
- Leopold, K., Michalik, B. and Wiegand, J. (2013) 'Availability of radium isotopes and heavy metals from scales and tailings of Polish hard coal mining', *Journal of Environmental Radioactivity*, Vol. 94, No. 3, pp.137–150.
- Mahieux, P.Y., Aubert, J.E., Cyr, M., Coutand, M. and Husson, B. (2010) 'Quantitative mineralogical composition of complex mineral wastes – contribution of the Rietveld method', *Waste Management*, March, Vol. 30, No. 3, pp.378–388.
- Matýšek, D., Jirásek, J., Osovský, M. and Skupien, P. (2014) 'Minerals formed by the weathering of sulfides in miners of the Czech part of the Upper Silesian Basin', *Mineral. Mag.*, October, Vol. 78, No. 5, pp.1265–1286.
- Matyskin, A.V., Ebin, B., Allard, S., Torapava, N., Eriksson, L., Person, I. and Ekberg, C. (2017) *Crystal Structure of Radium Carbonate: An X-Ray Powder Diffraction, Extended X-Ray Absorption Fine Structure and Direct-Space Initio Study*, Manuscript Chalmers University of Technology, Sweden.
- Michalik, B. (2011) *Radioactive Contamination of Environment Caused by Activity of Underground Mines*, in Polish, Prace Naukowe GIG, No. 883, Katowice.
- Plewa, F. and Myslek, Z. (2001) 'Management of industrial waste in underground mining technologies', *Monograph*, in Polish, Publishing Silesian Univ. of Technology, Gliwice.
- Plewa, F., Popczyk, M. and Pierzyna, P. (2013) 'Application of selected power generation waste with an admixture of binder in solidifying backfill for underground mining', *Energy Policy*, Vol. 16, No. 4, pp.257–270.
- Proksa, J., Łączny, M. and Bzowski, Z. (2020) 'Evaluation of the possibility of using granulated carbonated volatile fly ash from fluidized bed (G-CVFA) in underground mining techniques', *Archives of Mining Sciences*, Vol. 65, No. 4, pp.737–750.
- Ren, Z., Yu, F., Gao, H., Chen, Z., Peng, Y. and Liu, L. (2017) 'Selective separation of fluorite, baryte and calcite with valonea extract and sodium fluosilicate as depressants', *Minerals*, Vol. 7, No. 24, pp.1–12.
- Rietveld, H.M. (1969) 'A profile refinement method for nuclear and magnetic structures', *Journal of Applied Crystallography*, No. 2, pp.65–71.

- Rodriguez-Carvajal, J. (1997) 'Structural analysis from power diffraction data the Rietveld method', in *Proc. Ecole Cristallographie et Neutrons*, Paris.
- Torapava, N., Ramebäck, H., Curti, E., Lagerkvist, P. and Ekberg, C. (2014) 'Recrystallization of  $^{223}\text{Ra}$  with barium sulfate', *Journal of Radioanalytical and Nuclear Chemistry*, Vol. 301, pp.545–553.
- UNSCEAR (2000) *Report to the General Assembly with Scientific Annexes. Sources and Effects of Ionising Radiation*, United Nations Scientific Committee on the Effects of Atomic Radiation, UN Sales Publication E.00.IX.3, New York, UN.
- Vinograd, V.L., Kulik, D.A., Brandt, F., Klinkenberg, M., Weber, J., Winkler, B. and Bosbach, D. (2018) 'Thermodynamics of the solid solution – aqueous solution system  $(\text{Ba}, \text{Sr}, \text{Ra})\text{SO}_4 + \text{H}_2\text{O}$ : I. The effect of strontium content on radium uptake by baryte', *Applied Geochemistry*, Vol. 89, pp.59–74.
- Wysocka, M., Chałupnik, S., Chmielewska, I., Janson, E., Radziejowski, W. and Samolej, K. (2019) 'Natural radioactivity in Polish coal mines – an attempt to assess the trend of radium release into the environment', *Mine Water and the Environment*, Vol. 38, No. 3, pp.581–589.
- Zielinski, R.A., Otton, J.K. and Budahn, J.R. (2001) 'Use of radium isotopes to determine the age and origin of radioactive barite at oil-field production sites', *Environmental Pollution*, Vol. 113, pp.299–309.