Purification of Saline Waters from Coal Mines from Radium and Barium

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ABSTRACT

In underground coal mines in the Upper Silesian Coal Basin there are inflows of highly mineralized waters containing radium and barium ions. These waters cause radioactive pollution of the natural environment in mining areas and cause very serious technical problems, because thick layers of hard deposited $BaSO_4$+$RaSO_4$ cover the inner surfaces of pipelines and pumps. Therefore cleaning of saline waters of barium and radium is very important.

A very efficient and inexpensive method of purification of saline waters of Ba^{2+} and Ra^{2+} ions is described. Laboratory and field experiments were performed. For purification of saline waters - waste products from other industrial processes are applied. The method of purification has been applied at full technical scale in two collieries with very good results. In another two collieries cleaning processes will be started in the next year. Purification takes place in underground old workings without any contact of mining crew with radioactive deposits. As a result the amount of radium released to the natural environment was significantly diminished - approximately 130 MBq of ^{226}Ra per day and a similar amount of ^{228}Ra.

Another type of radium waters does not contain barium ions but contains SO_4^{2-}. There is no carrier for radium coprecipitation and radium is transported with discharge waters to the main rivers. Different methods of purificaton from radium must be applied for such waters. Laboratory tests and underground experiments have been undertaken with good results.

INTRODUCTION

Saline waters released from coal mines in Upper Silesia cause serious damage to the natural environment. First of all their mineralization is usually much higher than that of sea waters and may reach as much as 220 g/l. Moreover, the amount of these waters released from mines is very high. It varies from about 1 m^3/min to 30 m^3/min for different mines. The total output of Cl^- with waste waters from coal mines in Poland is of about $2*10^6$ tonnes per year. Unfortunately up to now only one water desalination plant exists, which utilizes 2000 m^3 of water per day. The remaining saline waters go to rivers.

Saline waters from Upper Silesian coal mines are often radium-bearing [1, 2]. Concentration of ^{226}Ra in natural waters occurring in carboniferous formations may reach 390 kBq/m^3, while in waters pumped out from underground mines concentrations of ^{226}Ra may reach 20 kBq/m^3. These waters cause additional impact to the environment. Radium-bearing waters often also contain Ba^{2+} ions (so called waters type A), which concentration may reach over 1 g/l. From such waters radium is easily co precipitated with barium as $BaSO_4$+$RaSO_4$, when mixing with other waters containing SO_4^{2-} ions proceeds. As a result radioactive deposits are formed, causing radioactive contamination of the environment [3]. The contamination takes place mainly along-side water streams and little rivers into which radium-bearing waters are released.

The aim of this work was to develop a safe, efficient and inexpensive method of purification of radium-bearing saline waters from coal mines of radium and barium with underground storage of remaining radioactive deposits.

Different problems are connected with radium-bearing waters, which do not contain barium ions (waters type B). As a result of a carrier absence for coprecipitation of radium, dilution in main rivers and adsorption on a bottom sediments take place. Also for such waters a method of purification from radium has been developed and tested during laboratory and underground experiments.

Chemical compositions of a typical radium-bearing waters type A and type B from Upper Silesia are given in Table 1.

BASIC CONCEPT OF THE PURIFICATION METHOD

Since from waters type A (with barium) radium easily coprecipitated with barium as sulfates the easiest way of cleaning these waters is treatment by sulfates. Yet, the purification method must fulfill the following requirements:

a) final concentration of ^{226}Ra must be lower than 0.7 kBq/m^3, which is a permissible level for a waste waters, due to Polish regulations [4];
b) created solid radioactive wastes cannot cause any hazard to the natural environment;
c) the purification technology should be inexpensive and possible to apply in large scale;
d) purification of radium and barium should not worsen other parameters of the water;
e) the technology must be safe for the mine workers.

These requirements can be met by application of phosphogypsum or other industrial by-products containing slowly soluble sulfates.

Phosphogypsum is a waste product from phosphate fertilizer production. Since the amount of phosphogypsum produced is very large (in Poland about $4*10^6$ tones per year), disposal of phosphogypsum poses a serious problem. Therefore utilization of phosphogypsum is highly desirable.

The developed method consists of introducing solid or suspend in water phosphogypsum into the settlement tank in which the purification of water is intended to take place. For underground coal mines the best place for this process is the gobs. Therefore, if only there is a possible location in the colliery, so that no water hazard would be caused and the free volume of the gobs is sufficient, the purification of water from radium and barium is performed in gobs. If there is no such a possibility, the purification can be performed in underground water galleries.

Table 1. Typical chemical compound of mine waters type A and B

	type A	type B
Conductivity µS/cm	151000	91182
pH	7.25	7.65
TDS at 378K mg/dm^3	135461	91182
Ra-226 Bq/dm^3	62.764	3.449
Ra-228 Bq/dm^3	24.67	5.10
Cations		
Ca^{2+} mg/dm^3	6497	1844
Mg^{2+} mg/dm^3	3747	1980
Na^+ mg/dm^3	34715	28048
K^+ mg/dm^3	299.1	267.8
Fe mg/dm^3	<0.05	<0.05
Mn^{2+} mg/dm^3	<0.05	<0.05
Ba^{2+} mg/dm^3	1482	-
Total mg/dm^3	46740	32140
Anions		
Cl^- mg/dm^3	77352	50835
SO_4^{2-} mg/dm^3	0.0	2136
CO_3^{2-} mg/dm^3	0.0	0.0
HCO_3^- mg/dm^3	24.40	67.10
SiO_4^{4-} mg/dm^3	2.00	3.45
Br^- mg/dm^3	241.3	154.6
J^- mg/dm^3	10.90	11.20
Total mg/dm^3	77631	53208

Water to be cleaned of radium and barium is introduced into the settlement tank (gobs c water gallery), where mixing with phosphogypsum takes place. Barium and radium sulfate precipitate and settle onto the bottom. At the outlet a small water dam is placed. Water flowin out from the dam is free of radium and barium and usually also free of suspension. The additiona benefit of this method is that produced solid radioactive wastes remain in gobs and therefor does not cause any harm to the environment and to the staff. In the case when cleaning proces takes place in water galleries, created radioactive deposits are carried out and stored in gob using hydrotransport. So also in this case there is no radiation hazard to the miners.

Sometimes it is difficult to collect together all underground mine waters to be cleanec Nevertheless, additional cleaning can be performed in a settlement tank on the surface, where a mine waters are brought together. In this case, when the settlement tank is cleaned, deposits ar also located underground in mined out areas.

LABORATORY TESTS

Laboratory tests included:

- purification of standard Ba^{2+} and Ra^{2+} solution by means of main components of phosphogypsum [$CaSO_4*2H_2O$, $CaSO_4*1/2H_2O$, $CaSO_4$, $Ca_3(HPO_4)_2$];
- purification of radium-bearing mine water type A, by means of above mentioned reagents;
- purification of standard solution by means of phosphogypsum (of mineral apatite and organic phosphorite origin);
- purification of mine water, mentioned above, by means of phosphogypsum;
- purification of mine water by means of gypsum, by-product from saline water utilization plant.

The test included mixing during different time periods, in different temperature and by different pH values. Concentration of radium isotopes has been determined by liquid scintillation counting preceded by chemical separation [5]. Low background liquid scintillation spectrometer "Quantulus", Wallac Oy, has been used. Results presented on figures 1 and 2 show that the main role in purification plays $CaSO_4*2H_2O$. Anhydrite is less effective, which is probably caused by its lower solubility. $Ca_3(HPO_4)_2$ is much less effective, because produced radium and barium compounds are more soluble then sulfates. Phosphogypsum acts similarly as $CaSO_4*2H_2O$. The purification process goes faster at lower temperatures (10-20°C) due to higher solubility of gypsum. Mixing during 5 minutes was quite sufficient.

It has been found that about 25% excess of phosphogypsum over barium content was required for standard solution. For purification of mine water the excess must be even higher. This is probably due to the high mineralization of water and therefore high ionic strength of the solution and to presence of Sr^{2+} ions which also take part in the reaction. Thus, the required proportion of phosphogypsum and water must be set experimentally for each mine water to be cleaned.

FIELD EXPERIMENTS

Field experiments and first application of the developed purification method was performed in "Krupinski" colliery, which is located in southern part of USCB. The total inflow of water into workings of this mine is of about 5600 m^3/day. The Cl^- concentration in water pumped out to the surface is of about 40 g/l, ^{226}Ra and ^{228}Ra concentrations were respectively 22 kBq/m^3 and 14 kBq/m^3, Ba^{2+} concentration was about 316 mg/l and total dissolved solids concentration (TDS) was of about 65 g/l. Therefore the total output of ^{226}Ra from "Krupinski" colliery was 92 MBq/day, while total barium output was 1500 kg/day. Single water inflows into mine workings often contain more radium and barium. Maximum ^{226}Ra concentration found in this mine was of 79.6 kBq/m^3.

We want to focus our description mainly on our experiences in this colliery. The purification process was applied in two stages:

Fig 1. Cleaning of standard solution

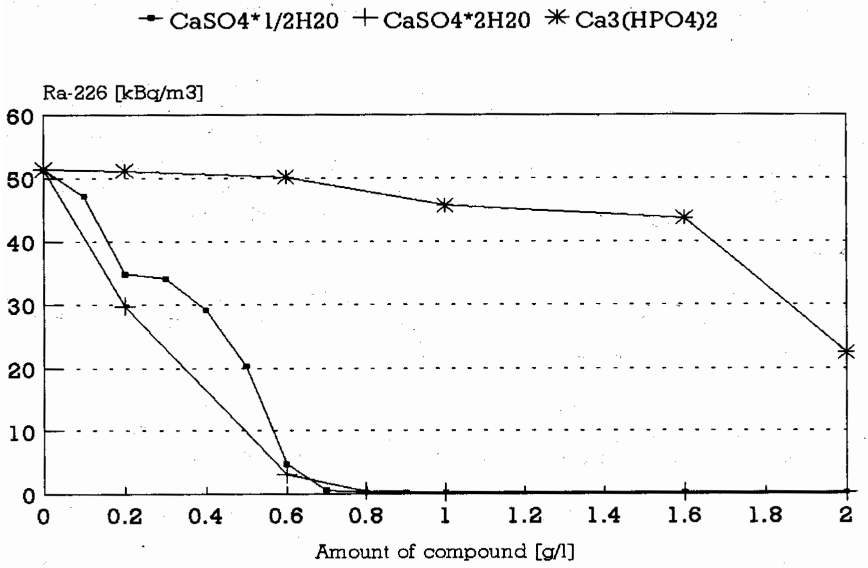
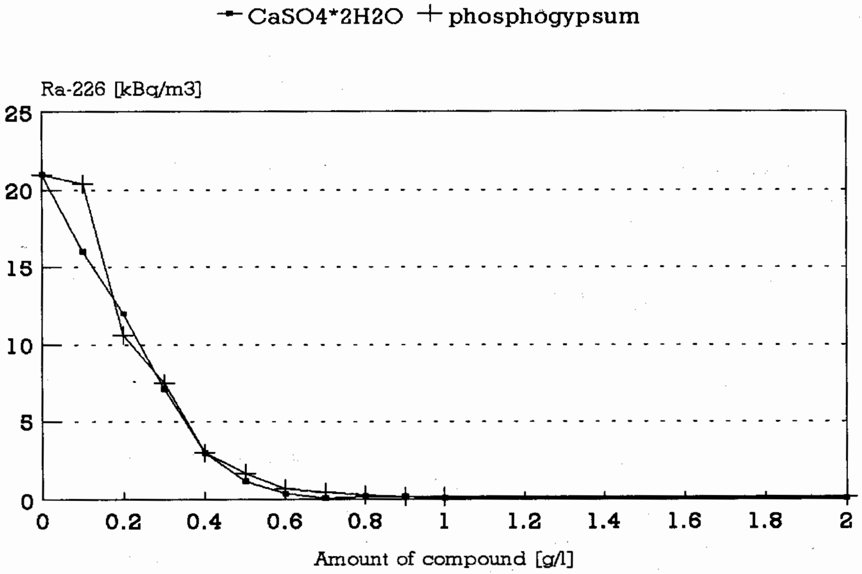


Fig.2. Cleaning of mine water



I Purification of all waters pumped out from the mine in a settlement pond located on the surface.

It was decided to start in June 1990 the purification process on the surface, because it was a much easier and cheaper way. Moreover, it enabled easier observation of the entire process. On the other hand, there was and urgent need of purification of waters of radium and barium, in order to avoid fines, which had to be paid according to a new radioactive waste materials act. Also waters from "Krupinski" colliery caused serious damage to the main pipelines leading saline waste waters from all coal mines located in the southern part of the coal basin, because of precipitation of $BaSO_4$.

The settlement tank is of 15000 m^3 of volume. Water is brought in from underground through 6 inlets, each of them goes through a little well and then to a gutter, from which is distributed evenly onto the whole width of the settlement pond.

Phosphogypsum was introduced into the above mentioned little wells in special baskets enabling washing out phosphogypsum by inflowing water. The reaction took place in the settlement pond. Clean water was pumped out by a regular system of pumps.

Results of purification during preliminary period are shown on fig. 4. As can be seen, during the first three months, the purification was not sufficient yet, but after adopting regular patterns of dosage of phosphogypsum and when the staff had become familiar and accustomed with the whole system of monitoring and control, good results have been achieved.

II Purification of radium-bearing waters underground.

This process was started four months after beginning the first stage cleaning, in November 1990. Gobs on level 620 m below surface have been chosen for this purpose. The schematic situation plan is shown on fig. 3.

Phosphogypsum is mixed with water in order to obtain fluid suspension, which is afterwards pumped periodically into gobs (gallery N-6), where water to be cleaned is lead. The mined out area, which was mined by a roof caving technique, serves as a settlement tank, where the reaction takes place and created $BaSO_4$+$RaSO_4$ settles down onto the bottom. The outlet of water free of radium and barium and to some extend also of suspension is located in gallery N-10, where a little dam is placed.

Then this water is pumped to water galleries on level 620m below the ground surface, where after mixing with the other mine waters and sedimentation of suspension is pumped out to the surface settlement pond, where the final cleaning takes place (see stage I).

Results of the cleaning process can be clearly seen. After stabilization of the underground cleaning process, water pumped out from the mine to the surface settlement pond contained much less of radium and barium (about 1.5 kBq/m^3 of ^{226}Ra and 40 mg/l of Ba^{2+}), but the concentration of radium was still higher than 0.7 kBq/m^3, which is the limit set by Polish regulations. This was because not all radium-bearing waters were collected together underground and purified. Nevertheless, final cleaning which was performed in the settlement pond on the surface, was quite sufficient to achieve good results, which can be seen on fig. 4.

Fig.3. Underground purification of radium in Krupinski Colliery

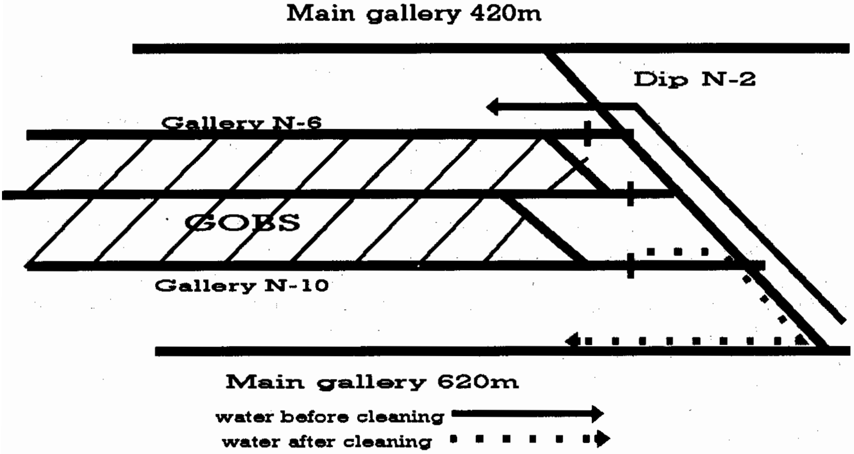
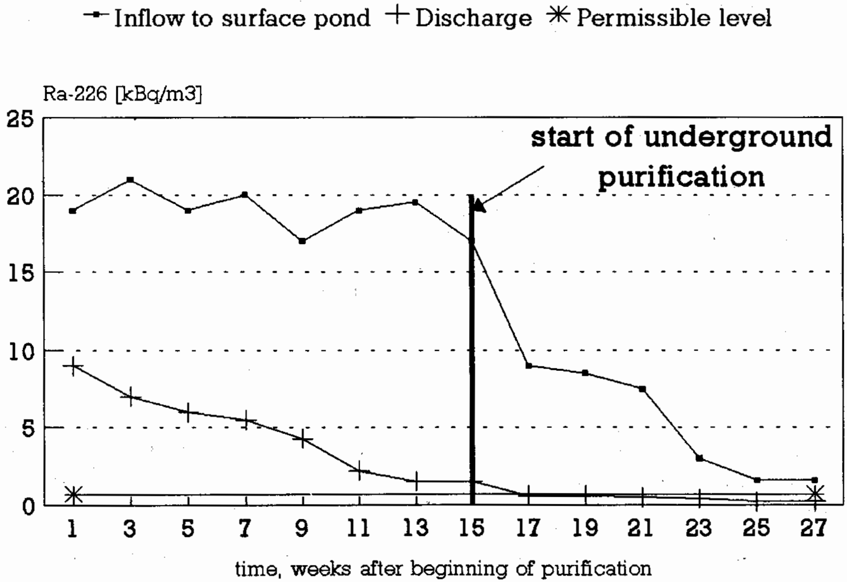


Fig.4. Field experiment - purification of mine water of radium in Krupinski Colliery



From the beginning of 1992 the next modification of cleaning process was undertaken. All radium-bearing waters are cleaned together, in the same place. A very good efficency of purification process have been achived (fig. 5.).

PURIFICATION IN "1 MAJA" COLLIERY

In 1991 a purification process has been started in "1 Maja" colliery. This mine released approximately 2000 m^3/day with ^{226}Ra concentration up to 20 kBq/m^3 and with barium content up to 2 g/l. Total output from mine was of about 40 MBq of ^{226}Ra and 600 kg/day of barium.

Unfortunately in "1 Maja" mine, there were no possibilities to find any underground gobs system, suitable for purification. Therefore water galleries have been used for water cleaning. Also, due to small volume of settlement tanks on surface, additional purification on surface was more difficult. At the beginning, results of purification were quite promising (see fig.6.), but during 1993 "1 Maja" colliery faced a new problem. Results of purification worsened gradually. This problem having been caused by new inflows of saline waters, rich in radium and barium. It showed that the process of purification needs careful supervising. After increasing the amount of phospohogypsum added daily into the water galleries the concentration of radium fell down below a permissible level.

Because measurements of radium concentration in water are rather complicated and time consuming current monitoring of the process was difficult. On the other hand the staff of the colliery needs at least rough information of purification efficency very quickly. To solve this problem a qualitative analysis of barium concentration has been applied. Routine analysis of barium presence in water after purification of barium and radium are performed in the mine`s chemical laboratory, and results of such analysis can be stated as a indicatior of the effectiveness of the purification process.

PURIFICATION OF RADIUM-BEARING WATERS TYPE B

For another type of radium-bearing waters, which do not contain barium ions but contain SO_4^{2-}, a different method of purification has been developed [6]. Laboratory tests and underground experiments in one of the Polish coal mines has been achieved with very good results. Probably by 1996 the problem of radioactive contamination of natural environment, caused by radium-bearing waters from coal mines, will be definitely solved.

CONCLUSIONS AND FINAL REMARKS

Radium-bearing saline waters, containing also barium ions can be cleaned underground of radium and barium by means of media containing slowly soluble sulfates such as phosphogypsum. Since phosphogypsum is a troublesome waste material from fertilizer production, the developed method has the following main advantages for the natural environment:

- cleaning waters of toxic elements - in our case of about 130 MBq per day of ^{226}Ra, similar amount of ^{228}Ra and approximately 2000 kg of barium;

Fig.5. Purification of mine water of radium in Krupinski Colliery

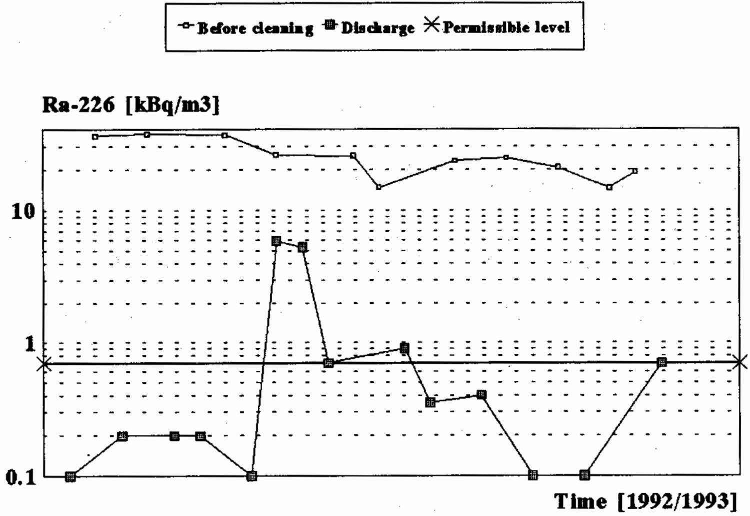
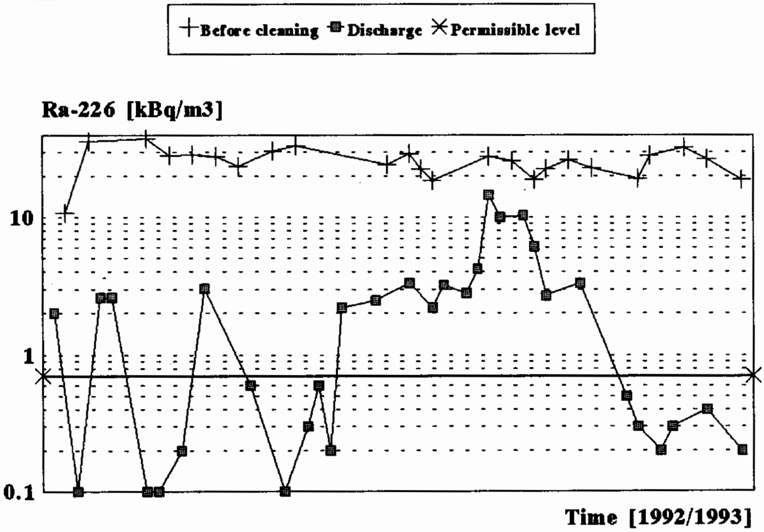


Fig.6. Purification of mine water of radium in 1 Maja Colliery



- storage of produced radioactive waste materials underground - more than 10000 tonnes of radioactive sediments per year with ^{226}Ra activity over 30000 Bq/kg;
- utilization of waste material from fertilizers industry.

The entire technology is inexpensive, very effective and applicable on a large scale.

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