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REDUCTION OF SULPHATE IONS CONCENTRATION IN DISCHARGE WATERS FROM Zn-Pb MINES

The paper presents a technological concept of limiting the concentrations of SO_4^{2-} ions in discharge waters from ore mines. It is based on authors' research performed for waters of Bytom trough, discharged on the surface in the volume of 30 thousand m^3/day. The method applied has been based on transferring SO_4^{2-} ions into a slightly soluble alkaline calcium-aluminium sulphate.

The technological concept assumes the following:
- use of the waste from anodic oxidation of aluminium (AUA) as a basic reagent in the process,
- conducting the reaction with AUA in a heterogeneous system,
- economic utilisation of post-process slime.

The results of laboratory tests indicate that the process will be feasible in practical use, and water will reach, after treatment, the quality corresponding with, at least, class III purity of surface waters.

Key words: calcium-aluminium sulphate, precipitation, environment, oxidation, surface water

INTRODUCTION

In the peak period of development of the mining industry in Poland, the mining-produced drainage was a source of water discharge amounting to 3 million m^3/day (GUS, Ochrona Środowiska, 1992). Such a scale of the phenomenon cannot be without consequence to the environment. The largest contribution to the stream of underground water discharged to surface water comes from hard coal mines. That is why in relation to them actions have been taken aimed at minimising the damages in the environment. The programme comprising research, design and development work resulted in the construction of two industrial installations for utilisation of underground water, functioning on the basis of different, original technological solutions (Motyka, Magdziorz, 1991). However, the diversified characteristics of waters from drainage of the exctractive industry mining various minerals, makes

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impossible to transfer, in a simple way, the experience gained by the hard coal mining industry into other branches of mining.

The ore mining industry, whose water discharge is considerably smaller, must search for other, own solutions. In this case, the discharge waters have their characteristics similar to the leaching solutions from waste storage yards produced by extractive or metallurgical industries. The fact should be emphasised that the abandonment of mining does not solve the problem of water discharge from the existing drainage.

From the Bytom trough, where there are no active zinc and lead mines any more, but yet the volume of 30 thousand m^3/day of water discharge resulting from ore mining is pumped up to the surface (Kropka et al. 1994; Hydrolog S.C. Operat 2000). The management of these waters had not been included in the R&D programmes, and still it is an open problem. The specificity of the applied technologies is a result of the properties of underground water and objectives to be obtained using the utilisation technologies. They are different than in the case of desalination of sea water, and in the case of water and sewage management.

The main pollution source of the Bytom trough discharge waters are the processes occurring in the rock mass and in the waste placed on the surface. In these processes, the ions of heavy metals and sulphates are mainly leached. Their concentrations exceed many times the level considered admissible for discharge into surface water courses. As far as the removal of heavy metal ions to the degree enabling to meet the admissible concentrations is solved using simple means of precipitation of hydroxides, then the reduction of sulphate concentration demands applying complicated technologies. In this material, the results are presented aimed at developing a technology for removal of SO_4^{2-} ions from water solutions through precipitating them in the form of basic calcium-aluminium sulphate. The process was realised with the use of the waste product from anodic oxidation produced in the plants manufacturing the elements of the so-called aluminium joinery.

It was assumed that, by using aluminium compounds in an alkali environment, it is possible to precipitate SO_4^{2-} ions through changing their concentration to a level legally acceptable for surface waters. To use this process in the discharge water utilisation technology, it must fulfil the following conditions:
• low cost of the principal reagent,
• non-complicated method of batching, conducting the reactions and separating their products,
• possibility to integrate the proposed process into the existing system.

It was assumed that the process is to be conducted in heterogeneous conditions, with the use of fine $Al(OH)_3$ sediment, being a waste from the electrochemical processing of aluminium elements. The investigations were aimed at elaborating the technological guidelines for the process of reducing SO_4^{2-} ions concentration in the discharge waters from the Bytom trough to a level enabling to discharge the treated water into the receiver.

METHODOLOGY OF TESTING AND DETERMINATION

MATERIALS

The underground water samples were randomly collected at the inflow to the pumping chamber located at Bolko shaft in Bytom, during the operation of pumps forcing water from water heading to the surface. These are waters coming entirely from natural inflow.

Table 1. Characteristic quality indices of raw underground water- Bolko shaft

Index	Unit	Concentration range
pH	-	7.05 – 7.39
SO_4^{2-}	mg/dm^3	930 -1150
Zn	mg/dm^3	8.34- 15.0
Pb	mg/dm^3	< 0.010- 0.098

The waste in the process of anodic oxidation of aluminium is further on called the AUA waste. The remainder, after the process of electrochemical processing of aluminium, is a used electrolyte, which is subject to neutralisation by means of NaOH up to pH = 7.0. The originating sediment containing, first of all, aluminium hydroxide is being dewatered in a filtration press up to the water content of 75%. Yearly, about 500 Mg of the sediment is produced, considered to be waste, for which one seeks for the possibility of use. In the natural and alkali conditions, this waste is insoluble in water. The waste samples collected from the filter were dried at 105^0C, after that they were crushed in a mechanical mortar. After crushing, the material was obtained having the grain size of less than 200μm. The derivatographic analyses of the AUA dried at 105^0C have shown that that its main component is $Al(OH)_3$. The concentration of aluminium in the AUA was 290 g/kg of dry matter.

In the tests, analytically pure calcium hydroxide was also used.

METHOD OF CONDUCTING THE TESTS

The experiments were conducted in the FLOCCULATOR 2000 apparatus, designed to carry out tests in the laboratory conditions. Six glass containers with individually controlled mixers have time control elements mounted on them. These are the timers and speed control units. This enables to set exact values of rotational velocity and duration of individual phases of the process. The volume of water samples was constant and equalled 1dm^3. The time of contact of reagents with water and their dose varied.

The process was conducted in three phases:

- fast mixing, up to pH = 11.5,
- slow mixing,
- sedimentation and crystallisation.

The cleaning efficiency of discharge water was determined on the basis of SO_4^{2-} concentration in the over-sediment water.

The analyses of the sediment originating in the process of discharge water cleaning were performed only in selected cases. The principal criterion of selection was the obtainment of satisfactory purity of the treated water.

RESULTS OF THE TESTS

The tests on sulphate precipitation, performed with the use of an AUA waste sample of 0.7÷0.9 g/dm^3, and time of contact of the sediment with the solution of ca. 1 h, gave no satisfactory results (Fig. 1).
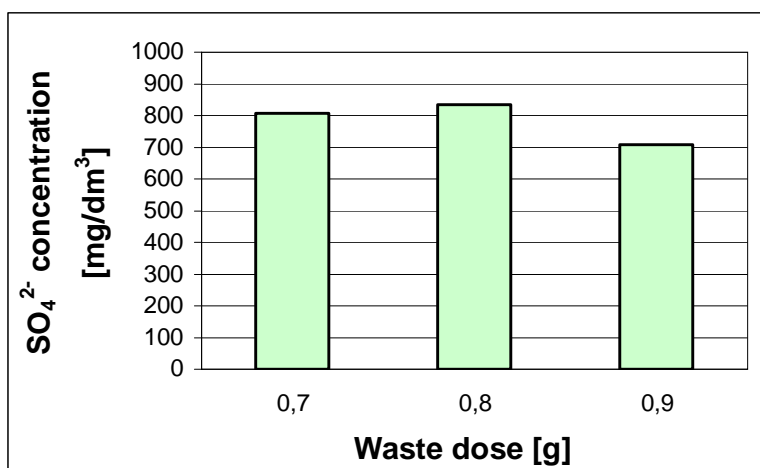

Fig. 1. Relationship between the dose of waste and final sulphate concentration. Initial sulphate concentration was 1034.3 mg/dm^3

The extension of used doses and time of contact leads to the results presented in Fig.2. The solid line in the figure correspond to linear correlation of measurement results.

In both tests performed, the 2 h time of free mixing was used. Of importance was the value of pH reached by the reaction mixture after fast mixing. It was found that the reaction is conditioned by reaching the value of pH of ca. 11.5. This condition is fulfilled when the $Ca(OH)_2$ dose equal to 4 g/dm^3 is used. It ensures effective precipitation of sulphate ions, while no effect of fast mixing time on the results of reaction are observed.
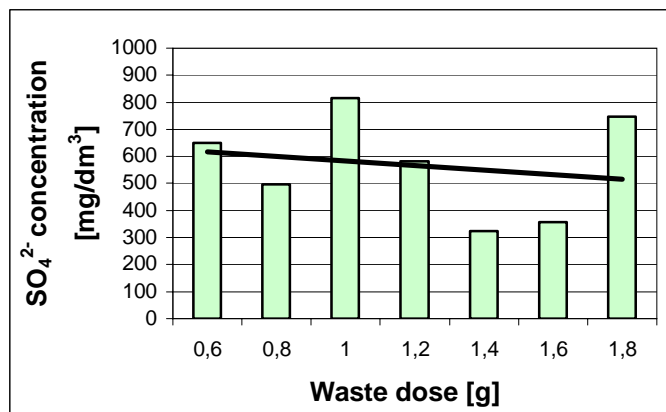
Fig. 2. Relationship between AUA dose and final sulphate concentration. Initial sulphate concentration was 930.6 mg/dm^3; time of contact 48 h

On the basis of multiple tests of precipitation of alkali calcium sulphate, the optimal doses of reagents being 4g Ca(OH)$_2$ and 1.6g AUA waste were confirmed. For such doses, the effectiveness of the process of SO$_4^{2-}$ removal from discharge waters proved to be the best.

The next parameter that affects the effectiveness of sulphate ions removal is the time of slow mixing. By using the most advantageous doses and extending the time of slow mixing, the results were obtained as shown in the diagram of Fig. 3.
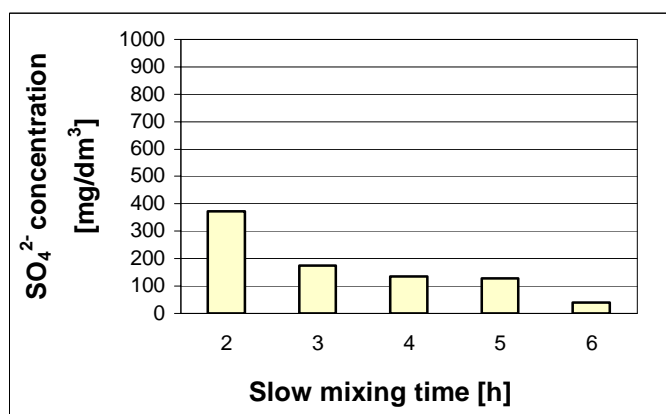

Fig. 3. Relationship between time of slow mixing and final sulphate concentration. 4 g/dm^3 Ca(OH)$_2$; AUA - waste 1.6 g/dm^3; initial sulphate concentration was 1045.0 mg/dm^3

The extension of slow mixing time to 6 h enabled to obtain an effective process of SO$_4^{2-}$ precipitation, without the need to apply a long time of contact of the sediment with over-sediment water. The time was shortened to 1 h.

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Using the 1.6 g AUA dose and extending the slow mixing time up to 6 h makes it possible to reduce the $Ca(OH)_2$ dose to 3.5 g/dm^3 without worsening the effectiveness of the process of water cleaning from sulphates (Fig. 4).
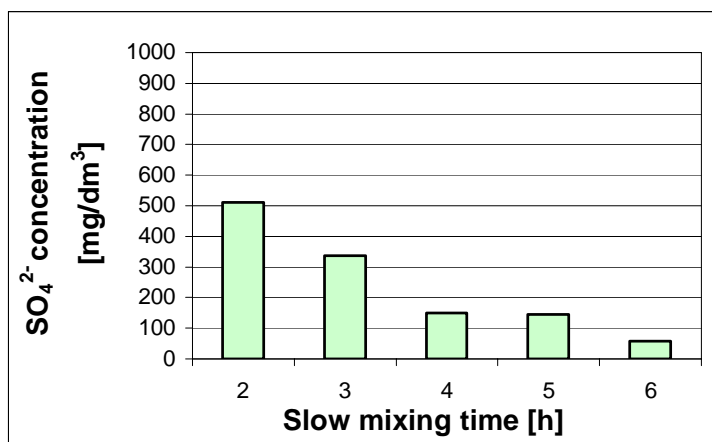
Fig. 4. Relationship between time of slow mixing and final sulphate concentration. 3.5 g/dm^3 $Ca(OH)_2$; AUA - waste 1.6 g/dm^3 ; initial sulphate concentration was 1045.0 mg/dm^3

The properties of the AUA waste, which is insoluble in the process conditions, allow supposing that the reaction proceeds close to its surface. The scanning picture of the originating solid product (Fig. 5) confirms the existence in it of hexagonal forms of aluminium-calcium monosulphate.
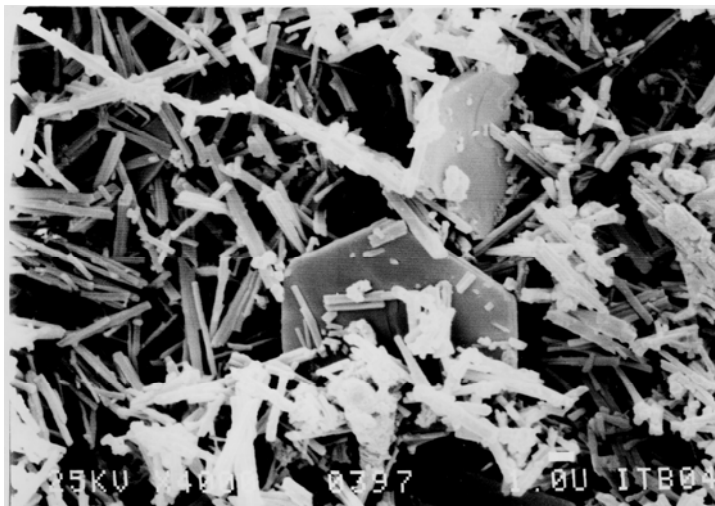
Fig. 5. Scanning photograph of process sediment; magnification x 1000

   The thermo gravimetric analysis (Fig.6) has revealed three characteristic decrements of mass. The first, in several stages, in the temperature range of 120 to 630 ^{0}C, is connected with the presence of crystalline water. It exists both in monosalt structures and ettringite, in the amounts greater than determined. The decrement of mass and endothermic curve in the temperature range of $660\div760$ ^{0}C are the diagnostic features of calcite. Its presence in the amount of ca. 20% confirms the fact that the creation of $CaCO_3$ is, in the process conditions, a competitive reaction to bonding of sulphate ions. The third peak, in the temperature range of $1200\div1300$ ^{0}C, is connected with decomposition of $CaSO_4$. The weight content of this component indicates that the SO_4^{2-} bond results mainly from creation of ettringite. In ettringite ($3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 32$ H_2O), the mass ratio of $CaSO_4$ to $3CaO\cdot Al_2O_3$ is 1.51. In the monosalt ($3CaO\cdot Al_2O_3\cdot CaSO_4\cdot 12$ H_2O) it is much lower, being 0.50. The result of thermo gravimetric analysis has revealed that in the tested material, the ratio of $CaSO_4$ to anhydrous remainder without calcite, is 0.93. Therefore, this is a proof for the question stating that the process proceeds mainly towards creation of ettringite.
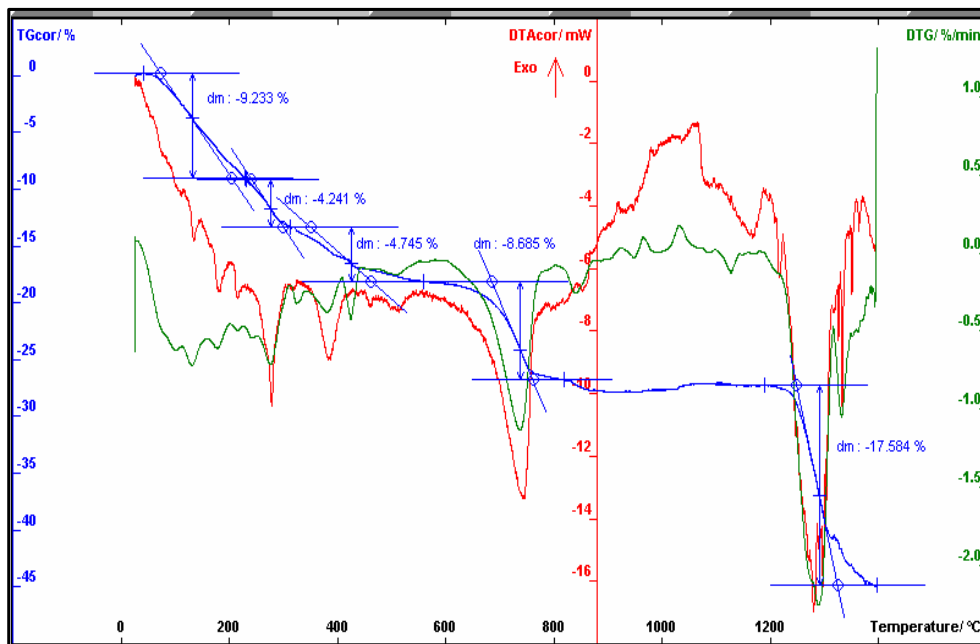

Fig.6. Derivatogram of a sediment sample after the process of discharge water cleaning with the use of AUA waste

   By applying the dose of 1.6 g AUA (876 mg Al_2O_3), it is possible to remove from it of ca. 1000 mg SO_4^{2-} (Figs. 3 and 4). This means that 1 mole of Al_2O_3 binds 1.22 of mole SO_4^{2-}. Such a result can be obtained when a part of sulphate ions is built in the ettringite structure. For practical application of the process, it is important that, as

early as after 2 hours of slow mixing, 60% of sulphates taking part in the reaction are removed. The elimination of next 40% of SO_4^{2-} ions requires to extend the time of slow mixing up to 6 h. In the over-sediment water $30 \div 100$ mg SO_4^{2-}/dm^3 remains. This justifies good effectiveness of the process of binding sulphate ions. This leads to the degree of cleaning which enables to discharge it into surface waters.

The investigations performed may be summarised with a proposal of a schematic technological diagram of cleaning waters discharged by Zn-Pb ore mines. This scheme, presented in Fig. 7, in a simplified way, gives the guidelines of the proposed technology. Batching of AUA and calcium hydroxide introduces minor change in the presently used scheme for water treatment. In respect of pH value of over-sediment water exceeding the standard, the scheme was extended with adding a process of saturation with carbon dioxide. Such a process is used in the technologies of water and sewage cleaning (Kowal, 1990). A source of CO_2 can be the atmospheric air.
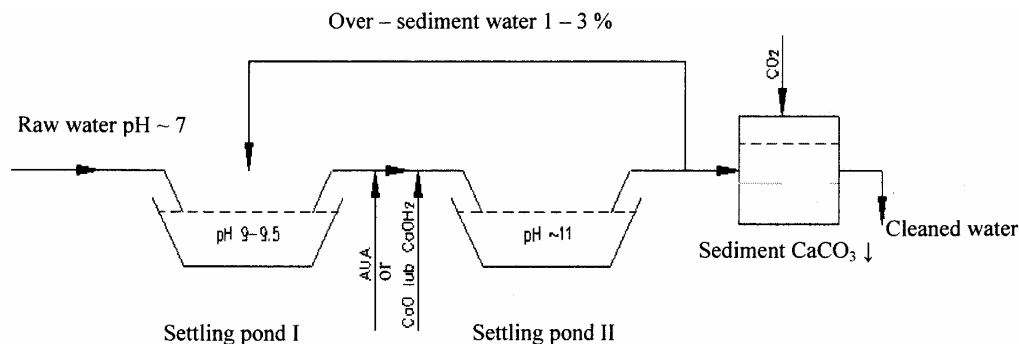

Fig.7. Schematic technological diagram for cleaning water discharged from Zn- Pb mines located in Bytom trough, using AUA waste

Fast and slow mixing in the laboratory conditions are a model reproduction of batching the reagents directly into the pipeline, under turbulent flow conditions, and then laminar flow in the settling pond.

Running the process of water utilisation in accordance with the technology presented schematically in Fig. 7 needs solving the question of management of the originating post - reaction sediment. For the sediment obtained in the investigations, the reactivity tests were performed (Szymanek, 2000) by determining the material capability of binding SO_2 from flue gas, presented in grams of S per kilogram of sorbent (Bis and Radecki, 2002). The obtained average result CI=136.6 gS/kg sorbent with the standard deviation of the average value σ_n= 19.2 points to excellent sorptive properties of the post-reaction sediment.

CONCLUSIONS

1. In the process of cleaning of underground water discharged from the Zn-Pb ore mines from SO_4^{2-} ions, it is possible to use, as an active reagent, the waste obtained after electrochemical treatment of aluminium (AUA) for which there is, so far, no idea of management.
2. The effectiveness of the process depends chiefly on bringing the reaction mixture to the required pH and time of slow mixing.
3. The process with the use of AUA waste is based on a heterogeneous reaction between the $Al(OH)_3$ sediment and water solution, and leads to origination of alkali calcium-aluminium sulphate, mainly ettringite.
4. The properties of sediments produced in the course of cleaning of underground water discharged from ore mines, with the use of AUA waste, point tothe possibility of their management as sorbents by dry methods of sulphur removal from flue gas.
5. The process water, because of its alkali character and high aluminium content, must be brought to the quality condition corresponding with the legal requirements, which demands applying individual technological solutions for each investment.

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W artykule zawarto założenia technologiczne procesu ograniczania stężeń jonów SO_4^{2-} w wodach zrzutowych kopalń rudnych. Oparto je na badaniach własnych wykonanych dla wód kopalń niecki bytomskiej, wyprowadzanych na powierzchnię w ilości do 30 tys. m^3/d. Zastosowano metodę polegającą na przeprowadzaniu jonów SO_4^{2-} w słabo rozpuszczalny alkaliczny siarczan wapniowo-glinowy.

Opracowana koncepcja technologiczna zakłada:
- użycie odpadu z anodowego utleniania aluminium (AUA) jako podstawowego reagenta w procesie,
- prowadzenie reakcji z AUA w układzie heterogenicznym,
- wykorzystanie gospodarcze osadu poprocesowego.

Rezultaty badań laboratoryjnych wykazują, że proces będzie możliwy w praktycznym stosowaniu, a woda po oczyszczeniu uzyska jakość odpowiadającą, co najmniej klasie III czystości wód powierzchniowych.