



Research on Purification Effect of Saline Mine Water from the Mines KGHM “Polska Miedź” S.A.

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Summary

Mine waters flowing into underground excavations of the mines which are included to KGHM „Polska Miedź” S.A. are characterized by diverse mineralization, hence the different utilization may be applied. In the major cases the mine waters are released directly or through sediment tanks to watercourses, which on the one hand increases the flow rate, on the other hand – taking into consideration high salinity (chlorides and sulfates charges) – cause degradation of water quality. In effect occurs deep and extensive transformation of water systems and downgrading of the environment in subsystems of groundwater and surface water.

The purpose of the studies was purification of mine waters from calcium, magnesium and heavy metals. In research on mine waters treatment membrane filtration, precipitation methods and ionite techniques were used. Applied methodology of removal of heavy metals from mine waters gave satisfactory results. All analyzed heavy metals have been removed to the assumed level. During the studies it was claimed that the precipitation of calcium and magnesium at the same time causes the precipitation of heavy metals. Because solubility equilibria of carbonates and hydroxides of heavy metals are much smaller than the solubility equilibria of calcium and magnesium carbonates, therefore heavy metals precipitate with them. Calcium and magnesium sediments are the media for precipitated heavy metals compounds. In addition, the presence of the carbonate ions derived from the dissolved calcium carbonate reduce the solubility of heavy metals carbonates. On this basis, it is proposed to apply precipitation of pollutants with sodium carbonate before filtration on ion-exchange bed. Such solution has two advantages. First, decreasing the content of heavy metals before ionite may lengthenworktime of bed between regenerations. Second, the lower the content of heavy metals in brine is, the more efficiently they will be removed by the ionite.

Keywords: rock salt, brine purification, ion exchange, heavy metals

Introduction

Mine water flowing into underground junctions in the mines that KGHM “Polska Miedź” S.A. (“Polish Copper” Co.) is comprised of, are characterized by diversified mineralization, thus they have varied uses. Water is mainly discharged directly or through settling tanks into surface water-courses, which on one hand, increases their intensity of flow, but on the other hand, because of high salinity (mainly charges of chlorides and sulfates), causes degradation of water quality. In effect, this leads to serious and widespread transformation of the water system and degradation of the environment in which the systems of underground and surface water flow operates.

From the point of view of legal provisions, water coming from mines, known as “dewatering”, is treated as waste.

Mine water in “Polska Miedź” S.A. mines

The following mines: “Lubin”, “Polkowice-Sieroszowice” and “Rudna” dispose of around 70-75 thousand m³/d of mine water, 95% of which 3-5 g/dm³ is saline, about 5%, which amounts to about 100-220 g/dm³. All mine water and waste from shafts’ sites goes through a flotation process, which ensures complete air-tight sealing of waste within the mines. The waste extracted via the flotation process is then discharged into a specially prepared storage yard. The main storage yard is “Żelazny Most”, which is used to deposit flotation waste and also for the retention of a sufficient quantity of industrial water for all the production plants. A system of pumping stations is then used for proper water distribution.

To preserve the salt and water balance, tens of thousands of cubic meters of water should be passed within a 24

hour period, of which over 20 g/dm³ is saline. The quantity of the water discharged corresponds to the current absorbing capacity of the Oder River so that after mixing, the total quantity of chlorides and sulfates in the Oder water does not exceed 1,000 mg/dm³. In 1997, a distribution system of discharged water was installed into a whole intersection of the river bed in order to minimize any locally increased salt concentrations in the river water. The quantity of suspended matter in the water carried away from the storage water area at “Żelazny Most” passed into the Oder is variable and depends mainly on the weather conditions., the purification plant is periodically turned on (based on coagulation process), in Therefore order to eliminate water discharges with excessive content of suspended matter.

Processes involved in copper ore treatment require, among other things, the use of large quantities of water – ca. 4-5 m³/Mg of ore feed for flotation. Flotation waste is ore pulp in a liquid state, where solids make up 6.5-8.7% of the volume. The waste is transported by pipelines to the storage yard at “Żelazny Most” (up until 1980, it was stored at the “Gilów” storage yard). In the storage yard, there is sedimentation of solids, and the clarified water is in-taken and re-directed to the Ore Concentration Plant. The water circulates permanently in the cycle between the Ore Concentration Plants and the storage yard.

Operation of the “Żelazny Most” storage yard

The yearly quantity of stored flotation waste fluctuates between 20 to 26 million Mg, almost 75% of which is used for further superstructure, and only 25% goes through the waste disposal process. Today, the “Żelazny Most” storage yard is the only place used for the storage of flotation waste for all of the KGHM “Polska Miedź” S.A. mines, which

Tab. 1 Ions content of heavy metals in mine water [mg/dm³]Tab. 1 Zawartość jonów metali w wodach dołowych [mg/dm³]

Designation	Content
Iron general	4.43
Calcium	6290
Magnesium	875
Manganese	1.82
Copper	4.89
Lead	12.10
Nickel	0.45
Chromium	0.25
Zinc	1.56

makes it a key technological element, without which the production of copper in the region would be impossible. Varying research has proved that the storage yard can cope with volumes of over 1.1 billion m³, which means it can cope with all water waste disposals until stocks of copper ore deposits in the Głogów Głęboki area are exhausted.

Apart from the basic function, which is waste utilization, the water basin constructed in the central part of the “Żelazny Most” storage yard functions as a settling tank for clarifying over-sedimentary water used in the cycle of flotation, and due to its vast volume as a storage reservoir, taking excess water used in the mine-process cycle. Excess water is sometimes carried away into the Oder by means of the hydraulic engineering (periodically) since 1978. The method was worked out and implemented by specialists from KGHM “Polska Miedź” S.A. in cooperation with various scientific centres. This system was implemented according to the legal provisions of the bill “Law of Water”, as an alternative method for the desalinations of certain kinds of mineralized water coming from mines.

Own research

While mining towards underground junctions, a large inflow of water with a varying degree salinity takes place. This water – according to the system of mining – is pumped out to the surface, where it is directed partially to the Oder, and partially to Ore Concentration Plants, where it is used for the flotation processes of copper ore.

This water contains many mineral compounds, including salts of heavy metals. Contamination by these compounds makes it impossible to use this water for the enrichment process. The research is looking into the possibility of purifying mine water of such undesirable compounds to a level enabling its further use.

Aim and subject of research

The aim of the research was to examine the possibility of removing ions of heavy metals from mine water.

The subject of the conducted research was the mine water collected in the pit bottom area of SW-1 shaft in the “Polkowice-Sieroszowice” mine, which is characterized by

a high level of salinity. Apart from the high content of sodium chloride found in this water, there are large quantities of calcium and magnesium salts, and also heavy metals. The level of heavy metal content exceeds the acceptable level many times in relation, not only to drinking water, but waste as well. In Table 1, the content of the heavy metals found in this mine water is presented. It should be pointed out that these values are not constant, but undergo periodical changes, which is most probably related to the opening of more and more mining fields in the copper ore bed.

Method of research

During the research on purifying the mine water of undesirable compounds and elements, the method of membrane filtration, precipitation methods and ionite techniques were used. Mine water was treated schematically as presented in Figure 1 and 2.

During the first stage, magnesium hydroxide and hydroxides of heavy metals were precipitated. To achieve the intended aim, a saturated sodium hydroxide solution was added to a sample of mine water in the quantity of 40 dm³, till pH > 10 was obtained. During the next stage, the solution with the jelly-like suspended matter was filtered on the membrane filtration equipment, in which ultra-filtration membranes with cut-off 100 kDa were used. Sample no 1 was taken from the filtrate, which was then analyzed.

The next stage was based on transmitting the obtained filtrate through ion-exchange bed with the aim of removing the remains of heavy metals. After transmitting through ion-exchange bed, filtrate sample no 2 was taken.

Simultaneously, the second analogous test – Figure 2 – was carried out with the quantity of the added sodium hydroxide solution, was to obtain pH = 9. The next steps were to filter through the ultra-filtration membrane, where the filtrate was directed to an ion-exchange bed. After the filtrate had gone through the ion-exchange bed, sample no 3 was taken.

To this purified mine water, saturated sodium carbonate solution was added in order to precipitate calcium ions and the remains of magnesium ions. This solution with the suspended matter underwent filtration processes through

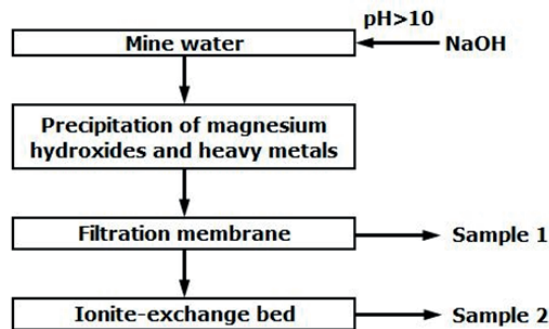


Fig. 1 Block scheme of mine water purification process – var. 1

Rys. 1 Schemat blokowy procesu oczyszczania wód dołowych – wariant 1

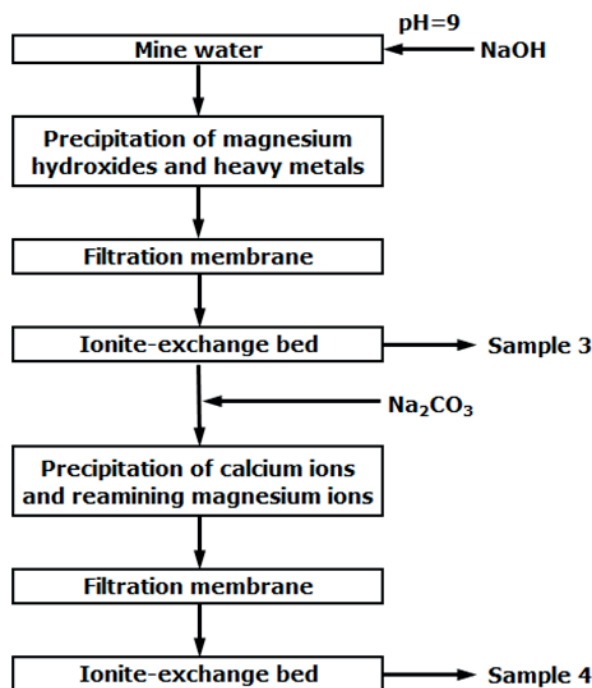


Fig. 2 Block scheme of mine water purification process – var. 2

Rys. 2 Schemat blokowy procesu oczyszczania wód dołowych – wariant 2

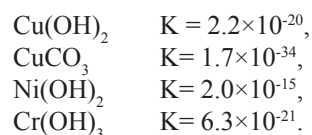
the membrane, and the obtained filtrate went again through the ion-exchange bed. From the mine water obtained, sample no 4 was taken.

Research results and conclusions

In Table 2, the results of the analysis of the mine water (raw) are presented, and after purification with the sorbent. On the grounds of the obtained analysis and results for individual samples taken during the research in progress, it can be stated that the assumed degree of heavy metals removal, has been achieved. The content of heavy metals in mine water changes between narrow limits, and the aim of the research was to check the efficiency of techniques for the removal of heavy metals from the ions.

The results from the analysis presented in Table 2 shows that pH value has a big influence on the degree of heavy metal removal and their content at the entrance to the ionite station. It is clearly seen in the case of copper,

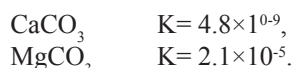
chromium and nickel ions. All the metals had already been removed from the tested solutions at the stage of calcium and magnesium precipitation below the level of determination. It results from solubility products of their hydroxides and carbonates, which appear as follows:



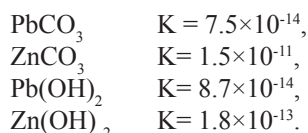
In addition, the precipitated magnesium hydroxide or calcium carbonate serves as a carrier, which increases the precipitation degree of heavy metals. At the same time, solubility products of hydroxides and carbonates of heavy metals are significantly lower than solubility products of calcium and magnesium hydroxides and carbonates:

Tab. 2 Results of mine water analysis after purification [mg/dm³]Tab. 2 Wyniki analizy próbek wód dołowych oraz solanki [mg/dm³]

	Sample no	Mg	CaCO ₃	Cu	Zn	Pb	Ni	Cr	Ag
var. 1 pH > 10	1	560	12482	<0.01	1.750	6.54	<0.005	<0.005	0.024
	2	486	3525	<0.01	0.228	<0.005	<0.005	<0.005	0.020
var. 2 pH = 9	3	384	11071	<0.01	0.184	0.033	<0.005	<0.005	0.036
	4	335	2718	<0.01	0.094	<0.005	0.002	<0.005	0.004



Due to that, the quantity of the precipitating agent added does not have any influence on the precipitation degree of these metals because the compounds of heavy metals are precipitated first. The precipitated carbonates and hydroxides of metals absorb into the carrier's surface, which is calcium and magnesium carbonates in this case. Some metals that have amphoteric properties behave a little differently, to which, in this case, belong: lead, zinc and chromium. The pH value is important in this case, which can be observed in sample no 1. After exceeding pH = 10, the reduction in zinc and lead content is low in comparison with the samples taken in different conditions, although the solubility products of their hydroxides are close to solubility products of copper:



It implies that part of hydroxides and carbonates of these metals went into the solutions in the form of plumbites and sodium zincates. However, this phenomenon has little influence on the stoppage of these metals on the ionite, which can be observed by analyzing the results for sample 3. In this case, a very big reduction in lead ion content is visible, from 6.54 ppm to 0.033 ppm, and zinc from 1.75 ppm to 0.184 ppm. This case demonstrates the effectiveness of complexing ionite, in case of exceeding solution pH value during the process of heavy metal precipitation such as lead, which are particularly dangerous for the health of people and animals.

Summary

Summing up the whole research, it can be stated that the research methodology used for heavy metal removal from mine water brought satisfactory findings. It can be stated that all analyzed heavy metals were removed to the assumed level. During the research, it was found that the precipitation of calcium and magnesium ions simultaneously causes the precipitation of heavy metals. This is due to the fact that the solubility products of carbonates and hydroxides of heavy metals are considerably lower than the solubility products of calcium and magnesium carbonates, thus heavy metals are co-precipitated with them. Deposits of calcium and magnesium compounds are, as it were, carriers for precipitated compounds of heavy metals, owing to which the removal degree of the latter increases. Additionally, the presence of carbon ions coming from dissolved calcium carbonates decreases the solubility of heavy metal carbonates. On the grounds of that, using precipitation of impurities by means of sodium carbonate was suggested before filtration in ion-exchange bed. Such a solution will bring double benefits. Firstly, the decrease in heavy metal content before the ionite will significantly extend deposit work-time between regenerations, thus the quantity of waste from the ionite regeneration will decrease. With the decrease in the total content of heavy metals below 0.5 ppm, the ionite work-time can last even up to a year. Secondly, the lower the content of heavy metals in salt water at the entrance to the ionite deposit, the more effectively they will be removed by the ionite. The pH value of salt water given to the ionite cannot exceed 10. After exceeding this value, part of heavy metal content changes into an anion form, and are not effectively stopped by this type of ionite. This fact particularly concerns such ions as lead and zinc.

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Badania nad oczyszczaniem wody kopalnianej z kopalni KGHM “Polska Miedź” S. A.

Wody kopalniane płynące pod terenami kopalni należących do KGHM “Polska Miedź” S. A. cechują się zróżnicowaną mineralizacją, stąd też podlegają różnym procesom utylizacyjnym. W większości przypadków wody kopalniane płyną bezpośrednio lub poprzez zbiorniki sedymentacyjne do cieków wodnych, które zwiększają wskaźnik przepływu, a drugiej strony – biorąc pod uwagę wysokie zasolenie (nasycone chlorkami i siarczkami) – powodują pogorszenie się jakości wody. W efekcie występuje głęboka i kompleksowa zmiana systemów wodnych oraz degradacja środowiska w zakresie wód gruntowych i powierzchniowych. Celem badania było oczyszczenie wód kopalnianych z wapnia, magnezu i metali ciężkich. Wody kopalniane poddano przetworzeniu przez membrany filtracyjne, metody uczestniczące oraz techniki jonizacyjne. Zastosowana metodologia usuwania metali ciężkich z wód kopalnianych przyniosła oczekiwane efekty. Wszystkie badane pierwiastki zostały obniżone do założonego wcześniej poziomu. Podczas analiz uznano, że wapń i magnez występuje równocześnie z metalami ciężkimi. Dzieje się tak ponieważ rozpuszczalność równowartych węgla, jak i wodorotlenków, metali ciężkich jest znacząco mniejsza niż rozpuszczalność równowartych wapieni i węglanów magnezu. Osady wapnia i magnezu są nośnikami związków metali ciężkich. W dodatku, obecność jonów węgla oderwanych z rozpuszczonego węglanu wapnia obniża rozpuszczalność węglanów metali ciężkich. Na tej podstawie zaproponowano dodanie zanieczyszczeń zawierających węglan sodu przed filtracją w procesie wymiany jonowej. Takie rozwiązanie ma dwie zalety. Po pierwsze, obniża zawartość metali ciężkich zanim jony zmniejszą okres pracy jonitu pomiędzy regeneracjami. Po drugie, im niższa zawartość metali ciężkich w solankach, tym skuteczniej zostaną one usunięte przez jonity.

Słowa kluczowe: sól kamienna, oczyszczanie solanki, wymiana jonowa, metale ciężkie