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IN-SITU LEACHING OF LIMESTONE IN THE PROCESS OF WATER DRAINAGE IN Zn-Pb ORE MINES

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Abstract: The necessary drainage and dewatering system of the exhausted and closed Zn-Pb ore mines in the Bytom area in Poland can be treated as a process of *in situ* leaching of sparingly soluble minerals from the disturbed rock mass. The slimes obtained from the discharged water treatment are considered to be useless material. Currently, their management only increases the cost of water drainage process. The lack of interest in the apparently unattractive market product, and certain formal resistance, result in the fact that the dewatering technological line has not been closed at a level of the intentionally conducted process of *in situ* leaching. The paper presents the authors' conception of winning useful, fine-grained limestone by modification of currently used technology of discharged water treatment from heavy metals (Zn, Pb and Cd). The essence of the process is receiving two products: cleaned water and mineral material having various possible applications.

Keywords: lead, zinc, fine-grained limestone, discharged water treatment, drainage, market product

Introduction

The recovery of any raw material is strictly related to the demand that results from its utilization in defined directions. This is, in the case of limestone, the demand of cement, limestone, iron and steel, refractive materials, and aggregate producing industries. One must also not omit the utilization of limestone as sorbents and fertilizers (Oliveira et al., 2014). In such applications, the material should be in a fine-size form. The prize of such a product depends greatly on necessity of comminution and milling.

The total production of useful minerals, chiefly limestone and dolomites in Poland, is approaching 50 Gg/year (Panstwowy Instytut Geologiczny, 2013; Główny Urząd Statystyczny, 2013). Such a production scale requires adequate cost of production and protection of environment. Neglecting the second element, it leads to the

consequences observed for instance in the Lagow Swietokrzyski (Poland) area which lost earlier values of clean environment as a consequence of intensive mining of limestone.

The extraction of limestone is generally conducted by surface mining. This system has been adopted as a consequence of low depth of deposit, and high rigidity of the limestone rock. In the case of need to obtain a fine-grained material, the cost of production and environmental protection increases. Any alternative solution is an action that saves the environment, and may also leads to reduction of production cost.

The paper presents a concept (Kupich et al., 2008) of a technology for winning fine-grained limestone, for which many possible applications have been indicated (Kupich et al., 2012). The proposed technology of *in situ* leaching has been used for many years for soluble salts (Poborska-Mlynarska, 2009; Kunstman et al., 2002). Under specific conditions of old, exhausted mines of the USA, Canada, and Spain, the *in situ* leaching had also been applied in the extraction of unrecoverable copper ore deposits (Marciniak-Kowalska, 1982, Sinclair et al., 2015). Hence, the capabilities of this kind of leaching should be verified in all the cases where the water infiltrating the detached rock renders, at the disposal site, sparingly soluble minerals. Their dissolution to the state of saturation is sometimes a long-standing process.

Principles of the process

The water penetrating the rock mass of the mines extracts carbonates, and then, due to the necessity of mine water drainage, is removed out to the surface. After having been cleaned, in order to reach the condition of being environmentally safe, water is directed to a receiver, usually river. When infiltrating the rock mass, water change its ionic composition that depends on the kind of contacted minerals. In the case of ore mines located in the Bytom trough in Poland, the velocity of the water stream increases at the last section of the flow through the mine workings. This results in liberation of fine grains. Cleaning of water is necessary before discharging into the Brynica river. The lime coagulation process is used for this purpose. The purification process is conducted by deposition of the suspensions, coagulation of colloids, and coprecipitation with CaCO_3 (Girczys et al., 2010). The main component of the slime released in the cleaning process is fine-grained calcium carbonate. It is obtained without the need of applying extraction and generating cost of milling and classification. The presented scheme of water circulation is the same as by *in situ* leaching (Rotuska et al., 2008). The innovation of the solution proposed for underground waters of closed ore mines in the Bytom trough (Kupich et al., 2008) is such collection and processing of the slime released from the solution that it should receive the characteristics of usable material having various possibilities of application (Kupich et al., 2012).

In spite of abandoning mining, the Zn - Pb ore mines in the Bytom trough are continually dewatered. It is conducted for the reasons of environmental safety and

protection of coal mines that extract the seams below the ore deposits. The slimes obtained from waters discharged by ore mines are considered to be useless. Currently, their management only increases the cost of the water drainage process. The lack of interest in the apparently unattractive market product, and certain formal resistance, results in the fact that the dewatering technological lines are not utilized properly.

Inflow waters of ore mines in the Bytom trough

The zinc and lead ore deposits in the Bytom trough are co-exist with the ore-bearing dolomite series of the middle Triassic. Connected with this is the richest underground Muschelkalk aquifer. The mining took place under the underground water level. In the eighties of the last century, a centralized water drainage system was adopted for the zinc and lead mines. The system relied on deepening one shaft (named Bolko), constructing a central pumping station and driving east-and westward water-drainage workings. The entire volume of waters from the areas, where the mining was finish after 1989, is directed to the central water drainage system at the Bolko shaft. The area of the Triassic Bytom reservoir is about 130 km². Its upper structural level is considered independent. It is located in the highly porous and fractured ore-bearing dolomites. It collects waters from the post-mining area and water contains dissolved components as a result of infiltration. The composition of water is formed through contact with waste deposited on dumps, triassic rock mass (disturbed as a consequence of extraction) in which chemical processes of oxidation and ionic exchange take place, and floor of the workings being troughs discharging water into the shaft sump.

The water from the central dewatering system of the ore mines, located in the Bytom trough, is pumped from the Bolko shaft sump into the settling pond at the surface. The main mineralization components of water discharged into the pond are the ions of calcium and HCO₃⁻. The pH of water is neutral while the carbonate concentration, being close to saturation, is at a level of 1480 mg/dm³. The average results of analyses of composition of discharged water in the Bytom area are presented in Table 1.

Table 1. Concentrations of pollutants in raw water from ZGH Orzeł Biały metal works, over the years 2004-2006, average value

Total suspension	pH	Hardness	Solid residue	Ca	Mn	Fe	Zn	Pb	Cd	SO ₄ ²⁻	Cl ⁻
mg/dm ³	-	mgCaCO ₃ /dm ³	mg/dm ³				mg/dm ³				
33.2	7.2	1479.5	2283.0	357.0	0.35	1.06	11.2	0.04	0.01	1072.5	227.9

The present technological system, used to process the mine-discharged waters, was mandated for reasons of safety and protection of the environment, the main reason being conditioning of underground water up to a level that meets the requirements for

waters to be discharged to the aqueous environment. However, it contains elements utilized in the processes of leaching both in dumps and in the deposit. The water circulation system has been built similarly to that utilized in leaching, e.g. of water in the deposits of exhausted mines (Ochromowicz et al., 2011). However, the components leached out and separated in the water treatment process have not become a market product, first of all because of their low price, formal objection, and lack of company that might be interested in starting production of slimes for specific use. The possibility of sending the waste sludge for use requires supplementing the existing technological system of the sewage dump with recovery of valuable components that is turning the waste into a product (Kupich et al. 2012).

Slimes released from Zn-Pb ore-mine discharge waters

Origin of slimes is a consequence of the need to dewater inactive zinc-lead ore mines from the Bytom trough. Cleaning waters before they are discharged into the Brynica river is performed through coagulation with lime. Lime milk is dosed directly to 600 mm in diameter pipelines through which mine water flows. It is delivered up to pH about 8.5. Both in the pipeline, and in the well before the settling ponds, intensive mixing with pumped out water takes place. The calcium carbide residue used for preparing the milk leads to the formation of very fine, difficult-to-settle, mixture. Therefore, the sedimentation is aided with polyelectrolytes. The amount of calcium carbide used is from 240 to 400 g/m³, which results in more than 10 Mg/day consumption. The chemical composition of calcium carbide residue is presented in Table 2.

Table 2. Chemical composition of calcium carbide residue used for coagulation (in weight per cent) (Kupich et al., 2008)

H ₂ O	Ca(OH) ₂	CaSO ₄	CaCO ₃	Zn	Pb	Fe	Cd	Mn	Ni	SiO ₂	Al ₂ O ₃
up to 20	84–90	0.5–3	5–9	0.003–0.007	0.02–0.5	0.1	0.0005	0.001–0.002	0.003	1–3	0.02–1

The slimes collected from the settling pond are alkaline. They contain about 90% of calcium carbonate and hydroxide. Mineral contamination of the sediment occurring in consequence of water convection, in the course of pumping water, are present depending on the quality of water drainage. The chemical analyses of slimes from discharge waters indicate their relatively stable composition. The results of the analyses are shown in Table 3.

The remaining components are present in minor amounts. Their concentrations determined from random analyses performed over a several-year period are: MgO 1.5%, Mn 0.22%, SiO₂ 3.4%, S 1.0%, Sb 0.015%, As 0.1%, and Cd 0.004%.

The main task of discharge water cleaning is to deliver pure water into the environment after separation from the sludge. Water then must have the characteristics of water neutral to the environment. This fact was confirmed in the tests made by the OBIKS in 1997. Despite a long term of storage and seasoning, the particle size distribution does not disqualify the possibility of using the slimes collected in the reservoir (Fig.1).

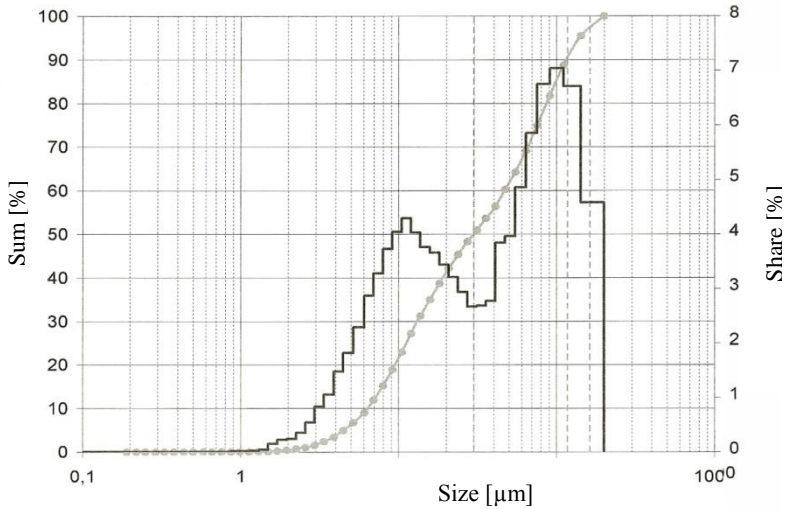


Fig. 1. Particle size composition of seasoned slime

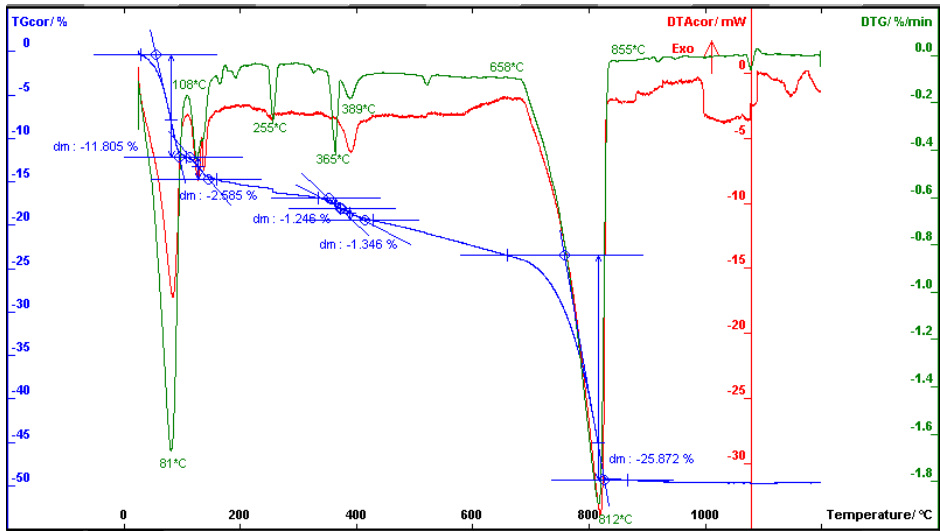


Fig. 2. Derivatographic analysis of seasoned slime

Table 3. Results of analyses of slimes after coagulation, converted to dry mass (% weight) (Kupich et al., 2008)

Ca(OH) ₂	CaCO ₃	CaSO ₄	Zn	Pb	Cu	Fe
14-15	60-85	5-7.5	1.7-4	0.05-1	0.002-0.008	0.4-1.3

The thermogravimetric analysis (Fig.2) has shown that the main components of the seasoned slime are: CaCO₃ (about 70%), Ca(OH)₂ (about 6%), Mg(OH)₂ (about 4.8%), and CaSO₄·H₂O (about 20%).

Discussion

The daily inflow of water into the workings of Polish mines in the Oder and Vistula rivers drainage basins reaches 3 Mm³. The third part of this inflow volume is water coming from the drainage of the workings of the coal mines. It was found that the hydrochemical character of water depended strongly on salt water discharge from the mines, which was the main factor disturbing the river natural environment (Jablonska, 2008).

The contribution of ore mine workings is much lower. In general, the common feature of the mine inflow is high mineralization of waters, resulting from the process conditions in which they originate. Depending on these conditions, they differ greatly with the concentration and sort of dissolved mineral substance. In the case of the most concentrated solutions, it is necessary to remove the mineral substance before the mine-drainage water is discharged into the rivers. Here, in an unintentional way, the process of in situ leaching in the deposit has been realized. As an example, one can quote the difficulties with introducing the water desalination products into the market from the installation at the Debiensko mine, operating for many years (Bobik et al., 2014). This is to be considered when searching for the possibilities of using the slimes from the treatment of waters discharged from Zn-Pb ore mines.

For the mines located in the Bytom trough, the proposition has been submitted to implement the process which the main elements includes the *in situ* leaching. Its result should be not only obtaining purified water but also standard-value products separated from the eluate, that is a fine-grained calcium carbonate of a special composition. The modification of the existing technological scheme should be made as a process oriented towards providing well defined characteristics of the final products. The product currently obtained may require only formal verification for several applications, for instance, applying for neutralization in the technology of obtaining zinc oxide from the acid charge, in the roll-down process, or as a sorbent to clean the exhaust gases in the same process.

The application of the dewatering system of the Zn-Pb ore mines to leaching of calcium carbonate was patented by Kupich et al., 2008. The scheme of the process is presented in Fig. 3.

Water from *in situ* leaching contains components that occur in the infiltrated material or those originating from redox reactions and ion exchange processes. Here, the equilibrium of carbonate-cationic state is reached, being specific for water in the investigated area (Girczys et al., 2010). The main component of the water solution is $\text{Ca}(\text{HCO}_3)_2$, originating as a consequence of water and carbon dioxide action on the limestone. This can be written as:



At a temperature of 20°C and pH about 7, the solubility of $\text{Ca}(\text{HCO}_3)_2$ in water reaches 1.66 g/dm^3 . Apart from high hardness of carbonate-rich water, the inflow water has a high concentration of pollutants in the form of metal-containing suspensions and solutions. The leached out calcium carbonate is obtained in the process which also cleans water from accompanying components. According to the solution presented schematically in Fig.1, the preliminary purification from the suspensions is made, traditionally, in water drainage system. The water liberated from natural suspensions is directed to a pumping station. Then, water is pumped to the settling pond at the surface. Just before the discharge to the pond, lime milk is dosed directly into the pipeline from the mixer. The milk is prepared from the calcium carbide residue (the main component is CaO) and raw mine water. The lime milk causes precipitation of metal hydroxides, coagulation aided with Ca^+ ions, and decarbonisation. Decarbonisation proceeds according to Eq. 2.



The CaCO_3 sediment originating from the decarbonisation reaction is collected by co-precipitation of the suspension, and as a partial solution, depositing in the form of slime in the settling pond.

In the case of overdosing waste lime, its surplus may be beneficial for the quality of the product obtained. The verification of this is however needed. When conducting the process at $\text{pH} \approx 9.3$ and 20°C , water with CaCO_3 concentration of about 15 mg/dm^3 was obtained. The remaining mass of carbonate precipitates as CaCO_3 . The over-sediment water from the settling pond is delivered to a receiver, that is the Brynica river. The slime from the settling pond is directed to the water drainage system. The process of dewatering and confectioning will be conducted upon the need of the recipient (drying, briquetting, comminution, storage, and portioning).

The decarbonisation process leads to slime having the properties of usable material, in the case when it is conducted with very hard water with $\text{Ca}(\text{HCO}_3)_2$ being close to saturation. The recorded long-term average of its concentration in the discharge water of the Bytom Trough remains at a level of $1480\text{ mg of CaCO}_3\text{ per dm}^3$, thus giving the hardness of 83°n . The calculation reveals that the hardness corresponding to $1000\text{ mg CaCO}_3/\text{dm}^3$ (56°n) with the discharge of cleaned water of about $20.000\text{ m}^3/\text{day}$

enables, as a result of a controlled process of lime coagulation, the production of calcium carbonate slime with a capacity of 7 Gg/year when converted to dry mass.

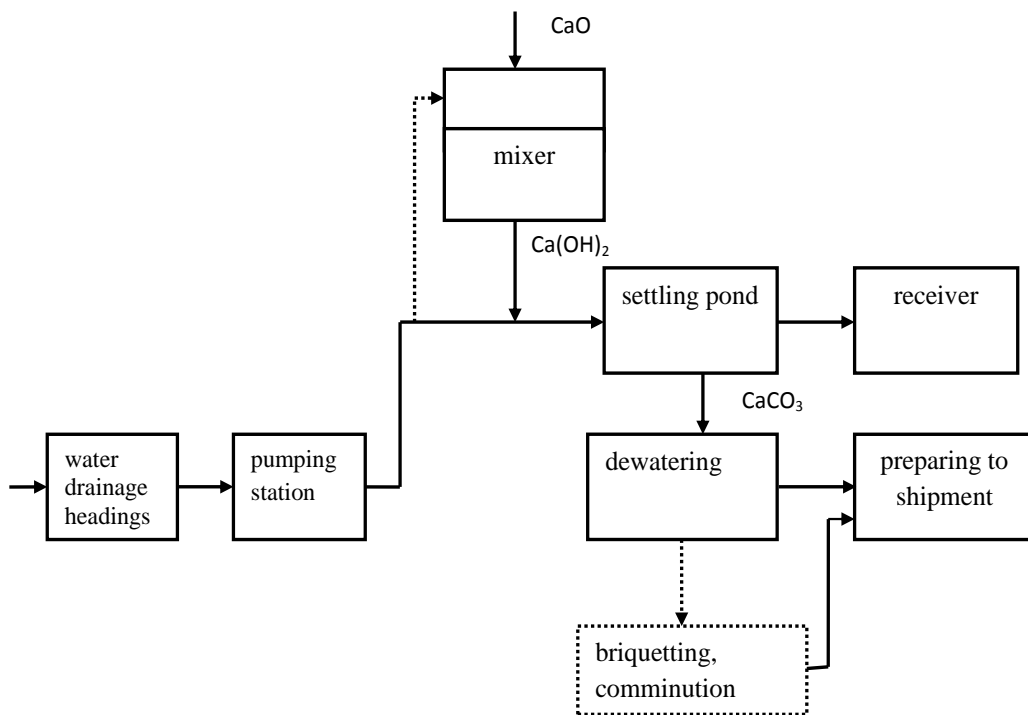


Fig. 3. Technology for utilization of fine-grained limestone (Kupich et al., 2012)

Conclusions

Dewatering of mine workings, in the case when the inflow water contains sufficiently high concentrations of dissolved minerals, or when these concentrations create hazards to the environment, may serve to obtain leached out substances. The essence of the process is receiving two product: cleaned water and mineral raw material to be used in specified applications.

Applying a mine drainage system as a process of leaching the rock mass minerals enables to obtain mineral raw material, in an environment-saving way, through no-waste management of the mine discharge waters. The waters inflowing the workings in the Bytom trough contain, as the main components: calcium - up to 400mg/dm^3 , magnesium - up to 150 mg/dm^3 , and zinc - about 10 mg/dm^3 , and they are accompanied by such anions as HCO_3^- and SO_4^{2-} .

Calcium carbonate from *in situ* leaching of the rock mass of ore mines, due to accompanying pollutants, has a beneficial chemical and grain-size composition,

particularly in application in the process of flame enrichment of an acid zinc-bearing charge in roll-down furnaces. Hence, the product obtained needs no expensive milling. Even after a long period of seasoning, the size composition is not subject to changes that might disqualify it in a given application.

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