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SLUDGE UTILIZATION OBTAINED FROM Zn-Pb MINE WATER TREATMENT

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The paper describes the possibilities for utilization of sludge obtained during the treatment of mine water discharged from the Zn-Pb ore mines. These possibilities were analyzed based on the results from the study on the properties of sludge from the treatment of mine water discharged from the mines of the Bytom Basin area. The fine-grained texture and chemical content of sludge result in the properties typical for very fine-grained limestone. Small quantities of unprocessed $Ca(OH)_2$ increase the activity of sludge in comparison to pure $CaCO_3$. Due to these properties the sludge may be applied in many environmental engineering processes aiming at limitation of heavy metal migration and SO_2 emissions, and also neutralization of waste acids from used accumulator processing.

key words: zinc and lead mining, water discharged, water treatment, sludge utilization

INTRODUCTION

The sludge from the treatment of water discharged from ore mining belongs to a specific category of waste and can often display significantly different properties. These differences are mainly the result of the diversity of the content of discharged water, and accordingly impose a suitable treatment method (Adamczyk, 1990; Adamczyk and Haładus, 1996; Kropka, 1995; Kryza at al., 1995). However, since the main goal of treatment is to discharge the water to the environment in a safe manner, it is expected that the sludge produced during mechanical separation should also be environmentally safe. This assumption was verified by the study of sludge from the treatment facility for mine water discharged from the "Bolko" shaft. Water subjected to treatment in this facility comes from drainage caused by the closed ore mines lo-

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cated in the area of the Bytom Basin (Kropka at al., 1995; Kropka at al., 1994; Kropka, 1996).

The technology applied in the "Bolko" shaft generates about 2 Gg (2 000 tones) of sludge per year. The properties and chemical content of sludge are similar to the natural raw materials exploited for economic purposes. Based on those assumptions and current legal requirements the analysis of utilization methods for sludge from mine water treatment was performed. In view of physical and chemical properties of sludge only the main directions of sludge utilization were analyzed. The advantages of sludge utilization can be manifold, including limitation of natural resources exploitation, improvement of environment protection and reduction of landfill areas.

Production of the sludge is the consequence of the needs to dewater old and closed Zn-Pb ore mines located in the Bytom Basin.

THE ORIGIN OF SLUDGE

DISCHARGED WATER

It is estimated that about 370,000 m^3 of mine water per day is discharged from Zn-Pb ore mines in Poland. Approximately 45% of this quantity is used for drinking and industrial applications (Adamczyk, 1990; Adamczyk and Haładus, 1996; Kropka, 1997). Water discharged from the closed ore mines in the area of the Niecka Bytomska, which contributes to about 8% of total quantity of discharged mine water, does not comply with the standards for drinking and industrial water (Kropka, 1995; Grabowska and Sowa, 2000; Kupich, 2005). The sludge generated in the process of mine water treatment is discharged to the Brytnica River (Hydrolog S.C Operat…., 2000; Girczys and Sobik – Szołtysek, 2003).

Due to the formation of an extensive depression cone on the large areas of ore mining the chemical content of water undergoes changes including an increase in the concentration of different constituents, mainly sulfates, calcium and heavy metals (Girczys and Sobik – Szołtysek, 2002; Informacje i dokumentacje "Bolko"; GIG, 1994).

Migration of heavy metals is strongly affected by the geochemical properties of the environment in which underground water transport occurs. The occurrence of carbonate rocks (i.e. dolomite and limestone) causes slightly alkaline reaction, and thus in natural conditions the bicarbonate ions predominate (Girczys and Sobik – Szołtysek, 2002). Under specific conditions it leads to a significant reduction of heavy metal migration.

Sludge from the treatment process is loaded with substances which can infiltrate to water from the surface to the intake in the shaft sump. Therefore, it contains insignificant or trace quantities of constituents typical for a given mining area (Grabowska and Sowa, 1996; Różkowski and Ziemiański, 1995).

SLUDGE SEPARATION

The mine water discharged from the Bytom Basin is treated by means of coagulation with the application of lime carbide residue which as lime milk is fed into the mine water pipelines. Intensive stirring of lime milk with mine water occurs in the pipeline and the well below the settling tank. The water is then discharged to the settling tanks where the suspended matter in the water undergoes coagulation and sedimentation. The application of lime carbide residue in the process of mine water treatment generates significant quantities of suspension that is well dispersed and difficult to sediment. To shorten the time the process of clarification of treated water the polyelectrolyte S-216 was applied. After the completion of a working cycle the accumulated sludge is removed from the settling tank whereas cleared water is discharged through a set of drainage channels to the Brynica River (figure 1).

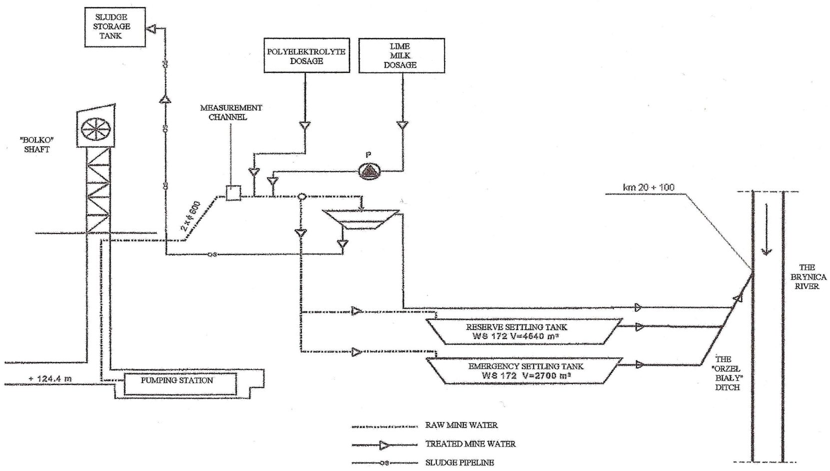

Fig. 1. Schematics of mine water discharge process

The content of lime carbide residue (dosed in a quantity of 250÷400 g/m^3) is presented in the table 1.

Due to the activity of lime carbide residue the water in the overfall of the settling tank is almost completely free of Pb, Cd and Cu. The concentration of Zn decreases from 12 mg/dm^3 in raw water to less then 2 mg/dm^3 in the overfall water.

Table 1. The content of lime carbide residue applied in the process of coagulation, (wt %)

H_2O	$Ca(OH)_2$	$CaSO_4$	$CaCO_3$	Pb	Fe	SiO_2	Al_2O_3
Up to 20	84÷90	0.5÷3	5÷9	0.02÷0,5	0.1	1÷3	0.02÷1

The addition of $Ca(OH)_2$ leads to the following chemical reactions:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O \tag{1}$$

and

$$Zn^{2+} + 2OH^- = Zn(OH)_2 \tag{2}$$

The main components of sludge are the calcium carbonate with the excess lime carbide residue formed during above reactions, and the suspended matters are. The sludge is a white, alkaline (pH ~ 9,8), and quite moist substances (40÷70%).

SLUDGE PROPERTIES

METHODS

The sludge separated from discharged water and the sludge water extracts were subjected to chemical analysis by atomic spectrometry methods (i.e. ICP and ASA). The phase composition was determined basing on the thermogravimetric analysis with a derivatograph (model Labsys, manufactured by SETARAM).

The analysis of grain size for material of the grain size < 200 μm was conducted by a laser grain size analyzer (model LAU – 10). Prior to this analysis the material with the grain size > 200 μm was removed.

The reactivity test (Szymanek 2000; Bis, Radecki 2002) was used to evaluate the potential of sludge as a sorbent for dry de-SO_x methods. This test allows to determine the absolute sorption (CI – capacity index) and reactivity of calcium sorbent (RI – reactivity index) indexes from the change in sulfur mass and content in the calcium sorbent exposed to exhaust gas containing CO_2, O_2 and SO_2 in the standard conditions. The total content of sulfur was determined with LECO SC-144 analyzer.

The absolute sorption index (CI) was calculated from [Alsthrom Pyropower…, 1995]:

$$CI = \frac{1000 \cdot \left[\frac{C_{S_p} - C_{S_b}}{100} + \frac{M_{CO_2}}{M_C} \left(\frac{C_{C_p} \cdot C_{S_b} - C_{C_b} \cdot C_{S_p}}{10000} \right) \right]}{1 - \frac{M_{CO_2}}{M_C} \cdot \frac{C_{C_p}}{100} - \frac{M_{SO_3}}{M_S} \cdot \frac{C_{S_p}}{100}} [gS/kg] \tag{3}$$

and the reactivity coefficient (RI) was calculated from [Alsthrom Pyropower…,1995]:

$$RI = \frac{\frac{C_{Ca}}{100} \cdot \frac{M_S}{M_{Ca}} \left(1 - \frac{M_{CO_2}}{M_C} \cdot \frac{C_{C_p}}{100} - \frac{M_{SO_3}}{M_S} \cdot \frac{C_{S_p}}{100}\right)}{\frac{C_{S_p} - C_{S_b}}{100} + \frac{M_{CO_2}}{M_C}\left(\frac{C_{C_p} \cdot C_{S_b} - C_{C_b} \cdot C_{S_p}}{10000}\right)} [mol\,Ca / mol\,S] \tag{4}$$

were:

C_{Ca}, C_{Cp}, C_{Sp}, C_{Cb}, C_{Sb} are the contents of calcium, carbon and sulfur in the sample after the test, carbon and sulfur before the test respectively [%],

$M_S, M_{Ca}, M_C, M_{CO_2}, M_{SO_3}$ - molar mass of sulfur (32,064 g/mol), calcium (40,08 g/mol), carbon (12,01 g/mol), carbon dioxide (44,01 g/mol), sulfur trioxide (80,06 g/mol).

The hydraulic permeability was determined from analysis of a seasoned sample of sludge (moisture content about 10%). An apparatus with a filtration chamber and a pressure tube was used to measure the velocity of filtration. The hydraulic permeability was calculated knowing the volume of the liquid in the pressure tube before and after each test in a given timeframe. The filtration coefficient for a given temperature (T) was calculated from:

$$k_T = \frac{a \cdot l}{A \cdot t} \log \frac{h_1}{h_2} \qquad [\text{m/s}] \tag{5}$$

where:

a – cross-sectional area of a tube, m^2,

l – height of a sample bed, m,

A – cross-sectional area of a sample, m^2,

t – filtration time, s,

h_1, h_2 – maximum and minimum levels of liquid in the tube (measured from the top level of the outlet), m.

RESULTS

Chemical and phase content

The results of tests performed are presented in the Table 2.

Table 2. The content of sludge after coagulation (d.m., wt %)

$Ca(OH)_2$	$CaCO_3$	$CaSO_4$	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 quantities of the remaining constituents are insignificant and the average contents determined by random tests in the past years are as follows (Table 2B):

Table 2B. The content of sludge after coagulation (d.m., wt %)

MgO	Mn	SiO_2	S	Sb	As	Cd
1.5	0.22	3.4	1.0	0.015	0.1	0.004

The water extracts of sludge was characterized by high alkalinity and low content of heavy metals. No trace of mercury was detected either in the sludge or in the water extracts, and the concentration of radionuclides was below the average content in the lithosphere.

The results of the tests did not confirm significant concentration of hazardous substances in the sample since those may be easily washed out to the environment. The concentrations of heavy metals are within the corresponding limits for first class inland surface water cleanness.

The data of the leaching test indicate an increased concentration of sulfates. The concentration was 3-fold higher than the corresponding standard limits for the wastewater discharged to water and soil.

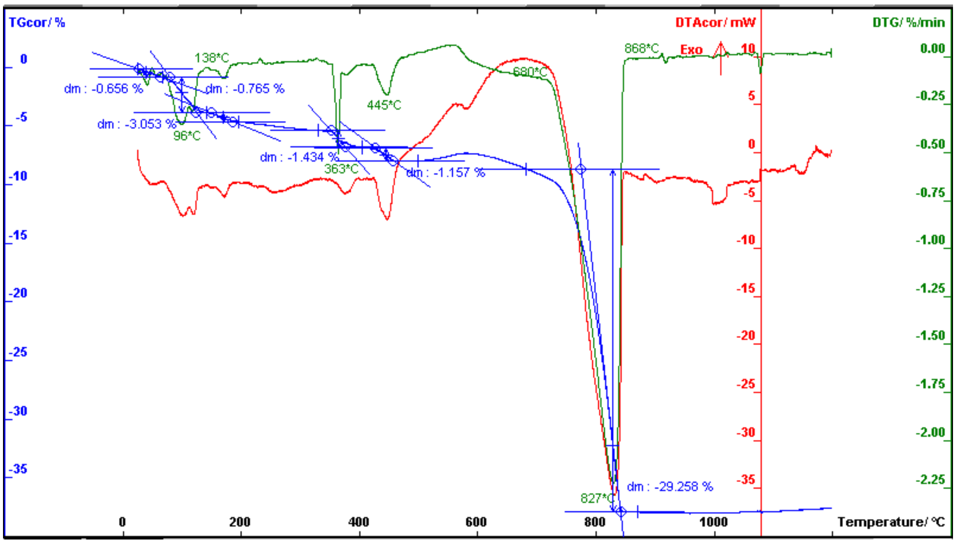

Fig. 2. Derivatographic analyses, sample No.1

The primary content of seasoned sludge samples in the settling tank during the recent years was determined by thermo gravimetric analysis and the results were presented in Table 3. The gravimetric transformations resulted from the effect of temperature on the sludge are shown in the Figure 3 (sample No. 1 sampled from the settling tank). With the reference to the thermo gravimetric data, the content of calcium hydroxide in the seasoned sludge sample (table 4) decreased at the expense of crystallization of gypsum, while the content of magnesium, as $Mg(OH)_2$, slightly increased (table 2).

Table 3. The content of the investigated samples (d.m.) – thermo gravimetric analysis

Sample No.	Ca CO_3 [%]	$Ca(OH)_2$ [%]	$Mg(OH)_2$ [%]	$CaSO_4{\cdot}2H_2O$ [%]	$Fe_2O_3{\cdot}H_2O$ [%]
1	70.22	5.07	4.86	15.42	4.43
2	60.53	6.44	4.03	29.0	-
3	72.95	6.92	4.96	15.26	-

With the reference to the thermo gravimetric data, the content of calcium hydroxide in the seasoned sludge sample (table 4) decreased at the expense of crystallization of gypsum, while the content of magnesium, as $Mg(OH)_2$, slightly increased (table 2).

Technical analysis

The investigated material was white, and the moisture retained under the intergranular pores was alkaline of pH~9,8. The results also demonstrated that the sludge was fine-grained. Prior to the analysis the sample was washed out and the fraction of material with the grain size > 200 μm (which was 3% of the total mass sample) was not typical for sludge separated during the treatment of discharged water, and thus removed. The grain size distribution for the sample No. 3 was presented in Figure 3 and is consistent with the results obtained for the remaining sludge sampled from the settling tank.

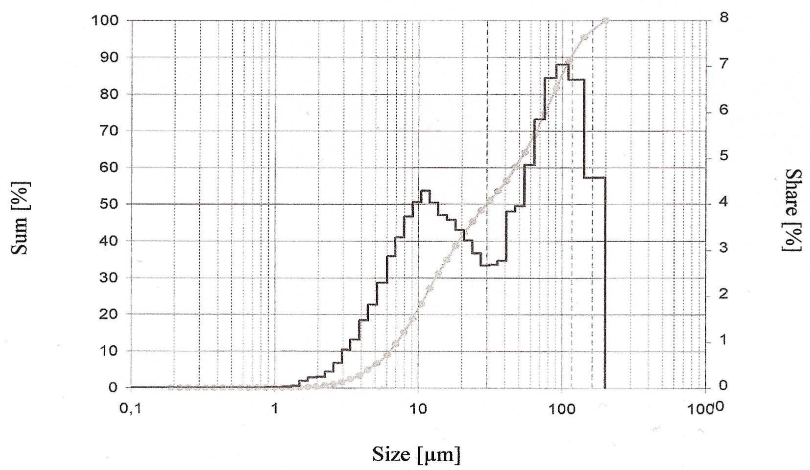

Fig. 3. Particle size distribution, sample No. 3

In the investigated material two fractions of particles of the size ~ 10 µm and 100 µm were observed. The fraction of grains with size less than 20 µm constituted over 40% of the total mass. This resulted in the expansion of the surface area estimated at about 2000 cm^2/g. The average grain density of ~ 2 g/cm^3 corresponds to the average grain size of ~ 15 µm.

Sorption capacity of sludge is one of the most important properties of this material. The chemical content and particle size distribution of sludge indicate that it may sorb heavy metals from solutions and SO_2 from gas phase. Even the total depletion of $Ca(OH)_2$, does not remove the sorptive properties, because $CaCO_3$ remains still active. The mechanism of heavy metals sorption in liquid phase is based on the processes of hydrolysis and dissociation, and can be described by a simplified equation:

$$CaCO_3 + 2\,H_2O \rightarrow H_2CO_3 + Ca^{2+} + 2\,OH^-. \qquad (6)$$

It has to be pointed out that this equation is general and all products in this reaction undergo further dissociation, hydrolysis and precipitation of slightly soluble compounds.

The carbonic acid dissociates according to the following equations:

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \quad K_1 = 4.5 \cdot 10^{-7} \qquad (7)$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \quad K_2 = 4.7 \cdot 10^{-11} \qquad (8)$$

The ionic activity of CO_3^{2-} calculated from Eqs 7 and 8 can be presented with the formula:

$$\log a\,(CO_3^{2-}) = 2\,pH + \log a\,(H_2CO_3) + \log K_1 K_2 \qquad (9)$$

In the state of equilibrium of the seasoned sludge sample (in which calcium carbonate is the main component) the pH was ≈ 9 and the activity (calculated from Eqs 6-8)
$a\,H_2CO_3 \approx 0{,}04$. Based on those calculations the activity of CO_3^{2-} (Eq. 9) becomes:

$$a\ CO_3^{2-} = 8.4\ .\ 10^{-3} \qquad (10)$$

Table 4. The results of sorption of seasoned sludge samples

Sample No.	RI [*mol Ca/mol S*]	CI [*gS /kg sorbent*]
1	4.1	57
2	4.5	51
3	4.2	55

This activity exceeds the solubility of the majority of heavy metal carbonates by several orders of magnitude. Therefore heavy metal ions precipitate and the concentration of those ions in the leachate is insignificant. However, high concentration of Ca^{2+}, Mg^{2+} and SO_4^{2-} ions is observed. The verification of SO_2 sorption in the gas phase indicated (Table 4) that the sludge produced during the treatment of discharged water is a promising SO_2 sorbent, even though some active substances were removed from sludge due to its storage in unfavorable conditions.

Hydraulic permeability

The hydraulic permeability of sludge was determined in the ambient temperature, and then recalculated to hydraulic permeability at 10 ºC. At this temperature the filtration coefficient was calculated from the formula:

$$k_{10} = \frac{1.359 \cdot k_T}{1 + 0.0337 \cdot T + 0.00022 \cdot T^2} \qquad [\mathrm{m/s}] \qquad (11)$$

The calculated coefficient of $7.0 \cdot 10^{-8}$ m/s was typical for powdery clay, aggregated mud and mudstone which are semi-permeable in horizontal and slightly insulating in vertical filtration (Marciniak et al., 1998). This combined with the sorptive properties makes sludge a perfect material for construction of active insulation barriers.

TECHNOLOGIES OF SLUDGE UTILIZATION

With the reference to the properties of sludge investigated in the presented study as well as the current state of legislation (Girczys, 2007; Prawo Ochrony Środowiska) several utilization technologies in which sludge can be a substitute for natural resources are suggested. The sludge generated in the treatment of mine water discharged from the „Bolko" shaft has properties similar to fine-grained limestone with small quantities of $Ca(OH)_2$, $Mg(OH)_2$ and iron hydroxides.

Suggested applications of sludge include three technological forms:

- an alkaline suspension for SO_2 sorption or H_2SO_4 neutralization
- an inert mineral layer for landfilling of various waste
- a filling material for post-mining voids or landfilling.

The first two forms can be obtained from sludge that was stored in conditions preventing from conversion of active substances into gypsum. Time for stabilization should not exceed several months. To ensure the required properties of sludge it should be extracted from a settling tank and air dried (e.g. under an umbrella roof).

The technology of wet removal of sulfur from exhaust gas is considered as the most technologically advanced. Sludge from the "Bolko" installation may be used for preparation of sorbent (Fig. 4). Without prior preparation sludge can be fed into a hydrocyclone (5) – unlike limestone it does not require milling. From the mine limestone is delivered to the warehouse by trains (1), and then it is transported by a belt conveyer to day storage bins (2) adjacent to the mills. From the day storage bins the limestone is fed to a ball grinder for grinding. Wet ball grinders are the most frequently applied. After grinding, the suspension with the limestone concentration of 70% is stored in a mill tank (4) where the suspension is diluted with water. Then, the suspension is transferred to a system of hydrocyclones (5) for grain size grading. Larger grains are fed back to the mill whereas the suspension with the required grain size is transferred to a buffer tank (6), then conveyed by a pipeline and fed to an absorber depending on, e.g. the concentration of SO_2 in the exhaust gas.

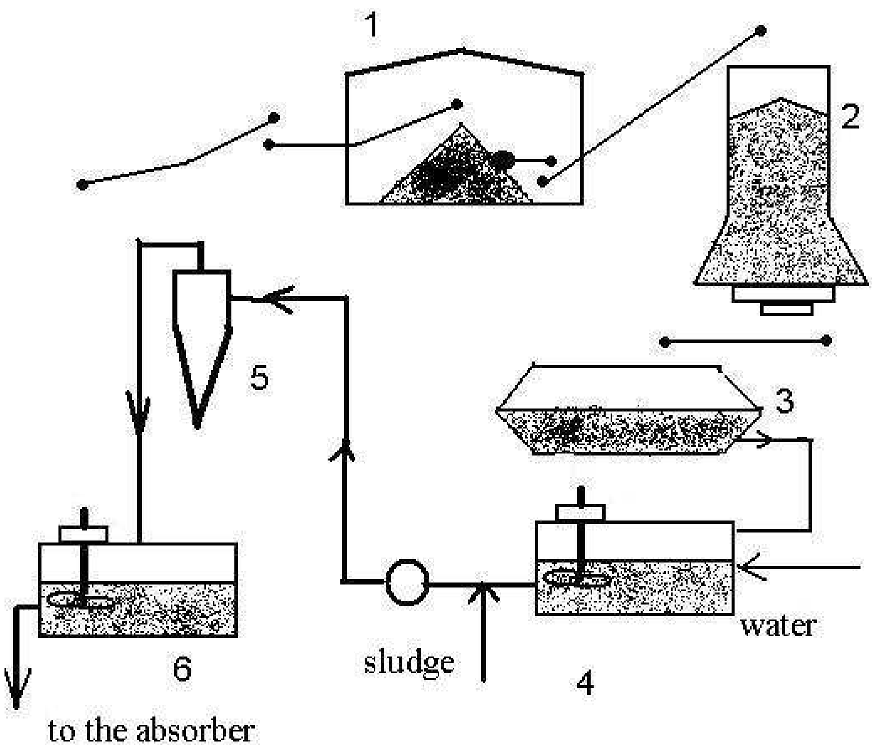

Fig. 4. Schematics of for limestone sorbent production technology

The sludge suspension also meets the requirements for alkalifying agents and can be used directly in the process of neutralization of sulfuric acid from used (old) car butteries (accumulators). The schematics of that process is shows in Fig. 5.

In landfilling municipal waste it is a prerequisite to apply inert layers in construction of a landfill. The layers can be made of debris, cullet, slag, ash, sand or other fine-grained mineral materials (Oleszkiewicz, 1999). Sludge from the “Bolko” shaft can be also used for building inert layers. Prior to this, the water needs to be removed to ensure proper distribution in the surface area. More over, the inert layers built with sludge can facilitate the processes of heavy metal sorption and alkalization of leachate.

The properties of sludge allow for technical reclamation of industrial waste landfills, particularly for construction of a subsoil inert layer. The primary operations in technical reclamation of existing dumping grounds include:

- land levelling to form the required shape of the surface
- compacting the upper layer (i.e. surface layer)
- applying a cover layer for plant vegetation.

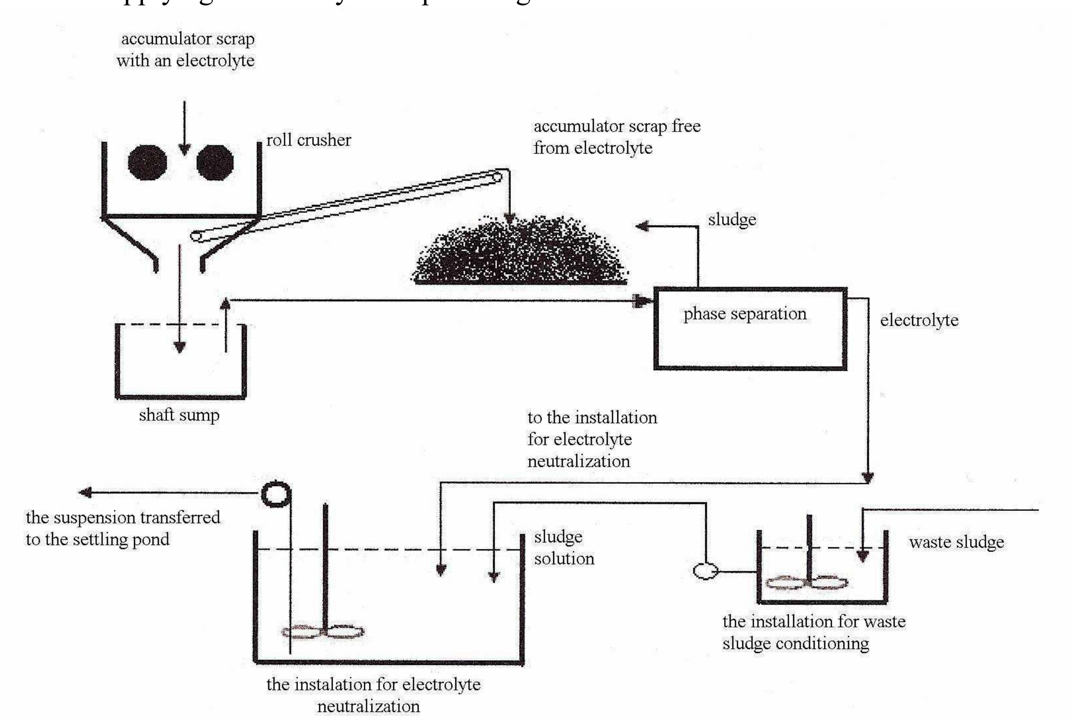

Fig. 5. Schematics of recovery and neutralization of sulfuric acid
from the used car batteries (accumulators)

Due to various properties sludge generated in the treatment of mine water can be used as a subsoil layer that insulates soil from the impact of hazardous waste and ensures proper conditions for plant vegetation.

Generally, the addition of sludge expands the area for landfilling and facilitates protection of the environment resulting from:

- improved compaction of waste in a landfill body
- favorable changes in chemical properties of a landfilled material.

The compaction of landfilled material can be improved by fulfilling the intergranular voids of waste coarse grain structure with sludge. This will efficiently reduce the processes of:

- water infiltration causing migration of metals

- oxidation leading to water and air contamination or even fires.

As a neutralizing material sludge can be applied for currently generated waste. Satisfactory results are achieved mainly in landfilling sludge blended with various types of slag, generated e.g. in the Dörschl's furnace, during melting of lead from accumulator scrap or ebonite from spent accumulator processing.

High quantities of $CaCO_3$, which constitutes about 80% of sludge dry matter, applied to waste with high content of heavy metals, allows for immobilization of these metals in the landfill body due to various chemical reactions. The value of solubility product for carbonates of heavy metals is lower by several orders of magnitude. This shifts the reaction equilibrium towards the formation of insoluble carbonates of these metals which are removed from infiltrating water.

The ratio of sludge and coarse grained waste in the mixtures depends on the size of intergranular voids. Sludge should be added in the quantity which allows to fulfill these voids. Under this condition the addition of sludge can be calculated from:

$$M_S = \frac{(\rho_W - \rho_N) \cdot \rho_S}{\rho_W} \tag{12}$$

where:

M_S – mass of sludge [Mg]
ρ_w – density of hazardous waste [Mg/m^3]
ρ_N – bulk density of hazardous waste [Mg/m^3]
ρ_S – density of sludge added to 1 m^3 of hazardous waste [Mg/m^3].

Another condition for estimating the ratio of sludge in mixtures is the content of $CaCO_3$. The addition of sludge should ensure that the quantity of $CaCO_3$, when dissolved in water, will balance stechiometrically all metals present in hazardous waste. This allows for efficient water protection in the infinite timeframe as the mechanism of carbonated mineral formation in nature (e.g. siderite, smithsonite, cerrusite) will be restored. Formation of these minerals in nature does not pose any threat to water.

CONCLUSIONS

The properties of sludge generated during coagulation of mine water discharged from the Zn-Pb ore mines were extensively studied. The knowledge of these properties allowed to develop suitable concepts for sludge utilization. It is estimated that the quantity of sludge generated annually in next few years will be at the same or slightly lower order than the current quantity. However, a due to silting-up, natural attenuation, formation of flow streams or technical activity in water regulation a strong tendency to reduce the quantity of sludge over time is expected.

In the view of the potentials for economic applications of the sludge the following conclusions may be formulated:

1. The sludge generated during treatment of mine water discharged from the “Bolko” shaft does not show any characteristics typical for hazardous waste.
2. With reference to the chemical composition and grain composition the sludge may be applied as a substitute of fine-grained limestone.
3. From technical and organizational point of view, the most suitable application of the sludge is its landfilling at areas designated for hazardous waste from used accumulator processing as an agent for removal of heavy metal ions from the car butteries (accumulators).
4. Another suitable application of the sludge is construction of mineral layers at municipal waste landfills. However, this can be done only at landfills employing advanced technologies.
5. The utilization of sludge for neutralization of a used electrolyte in butteries scrap processing does not require the implementation of new technical solutions. The sludge will partially substitute lime carbide residue.
6. After field-testing, sludge can be use as a SO_2 sorbent in sulfur removal from exhaust gas irrespective of applied technology.

The sludge can be also applied as a filling material for restoring post-mining voids. This should not pose any technical difficulties due the properties of sludge. However, prior to this application a number of formal requirements need to be fulfilled.

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Przedstawiono możliwości gospodarczego wykorzystania szlamów odpadowych z oczyszczania wód zrzutowych kopalń rud Zn-Pb. Samo wytwarzanie tego odpadu jest konsekwencją wynikającą z konieczności odwadniania nieczynnych już kopalń rud cynkowo-ołowiowych niecki bytomskiej. Przeznaczone do usunięcia z wody metale ciężkie, w wyniku hydrolizy i działania jonów węglanowych, występują w postaci cząsteczkowej, dlatego podstawą oczyszczania jest koagulacja wapnem. Ubocznym efektem tego procesu jest wytrącanie dużych ilości $CaCO_3$. Powstające osady mają właściwości fizyczne i skład chemiczny taki, jak materiały naturalne wykorzystywane gospodarczo.

Proponowane kierunki zagospodarowania szlamu mieszczą się w trzech grupach technologicznych:

- jako zawiesiny alkalicznej w sorpcji SO_2 lub neutralizacji H_2SO_4
- wykonywanie warstwy mineralnej, inertnej w stosunku do środowiska w procesie składowania różnych odpadów
- wypełnianie pustek poeksploatacyjnych górnictwa lub składowanie.

Wykorzystanie technologiczne odpadu z uzdatniania wód może przynieść wymierne oszczędności surowców naturalnych, poprawić warunki ochrony środowiska w obszarze składowisk i rozwiązać problemy z pozyskiwaniem terenu pod składowanie.

słowa kluczowe: górnictwo cynku i ołowiu, wody zrzutowe, uzdatnianie wody, utylizacja odpadów