

Original Research

Metals Recovery from Acid Mine Drainage and Possibilities for their Utilization

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Received: 26 March 2012

Accepted: 8 January 2013

Abstract

Extraction of coal, gold, and polymetallic ore, as well as their modifications, has left a lot of dumps of waste material, tailings, and abandoned mines in the world. Sulphide minerals in these deposits under aerobic conditions (air and water) are liable to microbio-chemical biodegradation by litotrophic bacteria and archaea, resulting in acid mine drainage (AMD) production. Processes caused by litotrophic microorganisms, namely *Acidithiobacillus* sp. and *Leptospirillum* sp. have occurred in the soil dump of pyritized hydroquartzite in the area of Banská Štiavnica – Šobov. They bring about AMD production, with dominant components of Fe, Al, and sulphates.

This article deals with active modification/treatment (gaining of Fe-sorbents, Fe-pigments) and remediation (decreasing concentration of contaminants – heavy metal, sulphate) of AMD from this area. The products of various purities, phase compositions, and properties, including surface properties, can be synthesized from AMD depending on the reaction conditions. Obtained Fe-oxyhydroxides can be transformed thermally to hematite structure (basic ferric pigment). The other method of utilizing of Fe-sludge is the creation of ferrites (general structure MFe_2O_4 ($M - Me^{+2}$), e. g. zinc ferrite).

In an application of alkaline industrial effluents, especially red mud bauxite and blast furnace slag, in batch experiment and neutralization of AMD, it has been shown that it is possible to reduce contents of Fe, Al, Cu, Zn, Mn, and sulphates with these agents.

Keywords: acid mine drainage, ferric pigments, adsorbent

Introduction

Acid mine drainage (AMD) and acid rock drainage (ARD) are both strong acidic waste waters rich on dissolved metal sulphates. They are formed in a complex process in which pyrite and other sulphide minerals, like pyrrholite, marcasite, chalkosite, covellite, and arsenopyrite, and chalcopyrite etc., in the presence of both oxygen and water as well as in the presence of acidophilic chemotroph-

ic bacteria and *Archaea*, mainly the genera *Acidithiobacillus*, *Leptospirillum*, *Sulfobacillus*, *Acidiphilium*, *Sulfolobus*, *Ferroplasma*, *Acidianus*, oxidize to produce dissolved metals, sulphate, and acidity [1-7]. AMD represents a serious environmental problem caused by mining activities (coal, gold, etc.).

Two main methods are described for AMD treatment. The first one exploits microbial remediation using acid reduction microorganisms in the sediment, resulting in a formation of metal sulphide precipitates [8-10]. The second solution uses passive or active treatment systems where the

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AMD is collected and chemically treated by neutralization of acidified effluent in a centralized treatment plant, constructed usually *in situ* or *ex situ*. Limestone, hydrated lime, soda ash – sodium carbonate, caustic soda – sodium hydroxide or ammonia are used as neutralization agents [11-14]. The AMD sludge contains a heterogeneous mixture of Fe and Al hydroxides, gypsum and other precipitated components of little practical value. To produce commercially usable iron oxides as a raw material for production of pigments, additives to ceramics, etc. by treating AMD, two-step processing of selective precipitation of hydroxides Fe and Al were developed [15-17]. The two-step process, using magnesium oxide and sodium hydroxide, results in the ferrous and ferric sludge for the synthesis of ferrites with magnetical properties, was developed for treating AMD from a gold mine [18, 19]. The ochre precipitation of AMD is a simplification as different solid phases are formed at different pH and sulphate concentrations [20, 21]. Schwertmannite [$\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4 \cdot n\text{H}_2\text{O}$] is the main phase when pH is in a range between 2.8-4.5, and sulphate concentration is in a range between 1-3 $\text{g} \cdot \text{dm}^{-3}$. Conditions for creating a mixture of schwertmannite and ferrihydrite ($\text{Fe}_2\text{O}_3 \cdot 1.8\text{H}_2\text{O}$ or $\text{Fe}(\text{OH})_3$) are: pH in a range between 2.8-4.5 and sulphate concentration higher than 1 $\text{g} \cdot \text{dm}^{-3}$. At higher pH ferrihydrite or mixture of both ferrihydrite and goethite ($\alpha\text{-FeOOH}$) precipitates are formed [22]. Mixtures of different minerals are often observed, partly due to transformation processes to thermodynamically more stable minerals. Aqueous precipitation is one of the most important unit operations for production of inorganic materials (pigments, catalysts, sorbents, etc.) or for immobilization of toxic inorganic waste, e.g. industrial effluent and waste water treatment [23]. Low cost sorbents such as coal fly, natural clinker, and synthetic zeolite were evaluated to clean-up and in particular to remove heavy metals and ammonium from AMD generated in a copper-lead-zinc deposit [24]. The experimental data reveal that heavy metal removal will depend on the sorbent material and on the applied dose. Natural clinker and probably coal fly ash did not show good efficiency as sorbent to neutralized AMD, but zeolites are beneficial products as ion exchangers in removing acidity, Fe, Zn, and Cu from AMD.

This paper summarizes the findings and results of the recovery of ferric oxides from AMD by selective fractionation, possibilities of transformation of ferric oxides to pigments, and treatment of AMD using some industrial effluents.

Materials and Methods

Chemicals and Solutions

NaOH, CaCO_3 , and ZnO were analytical grade chemicals provided by Sklo-Chem Zvolen, Slovakia. Red mud bauxite (RMB) was collected from ZSNP, A.S., Žiar nad Hronom and its composition is described in Table 1. Granulated and pumiceous blast furnace slag (BFS) in the form of fine powder was provided by Cement Works Lietavská Lúčka, A.S., Slovakia.

Table 1. Characteristics of RMB [25].

Component	Fe_2O_3	Al_2O_3	SiO_2	Na_2O	CaO	LOI*
Content [%]	30-35	16-20	8-13	2-10	4-12	8-12

*loss on ignition

Table 2. Characteristics of BFS (type JMT 350) [26].

Component	CaO	SiO_2	MgO	Al_2O_3	FeO	SO_4^{2-}	Humidity	LOI*
Content [%] max.	40	35	18	6	3	2.5	1	3

*loss on ignition

AMD samples were collected from the heap of quartzite from the mining area Banská Štiavnica – Malý Šobov, Slovakia [27]. The samples were filtered through a dense filter paper (Filtrak 390) and stored at 10°C. Properties of two AMD samples are summarized in Table 3.

Characteristics of Methods

Total content of iron and sulphate in AMD and in the mother liquid was determined by spectrophotometric method using α, α' -dipyridyl ($\text{LQ} = 0.04 \text{ mg} \cdot \text{dm}^{-3}$, $\text{RSD} = 3.2\%$) and by titration method using $\text{Pb}(\text{NO}_3)_2$ ($\text{RSD} = 1.1\%$). Other elements in the mother liquid and AMD and composition of solid products were determined at the Acme Analytical Laboratories (Vancouver), Ltd., by the ICP-ES/ICP-MS method, group water analysis 2CA, and by the ICP-ES method, group 1E (2009). Determination methods of specific surface area of Fe-precipitates (activation at 200°C in vacuum overnight) and X-ray diffraction analysis of ferrites were described previously [28, 29].

Preparative Methods

A. Recovery methods for the preparation of pure Fe-products from AMD using NaOH solution at 20-90°C

A solution of NaOH ($c = 2.27 \text{ mol} \cdot \text{dm}^{-3}$, adding rate = 2 $\text{ml} \cdot \text{min}^{-1}$) with continuous stirring at temperatures of 20, 40, 60, and 90°C, respectively, was added to 2 dm^3 of AMD. Values of pH and Fe concentrations were monitored in supernatant during the process. Precipitate formed at the decrease of Fe concentration below 10% from initial values (pH 2.9-3.2) was separated by vacuum filtration, washed with deionized water, and dried at 40°C.

B. Treatment and neutralization methods of AMD using solid components CaCO_3 , RMB, and BFS in a form of fine powder

Neutralizing agents were gently added to 5 dm^3 of AMD during continuous stirring until the pH values were in the range 6.8-7.1. Fe and sulphate concentration in supernatant were monitored during neutralization. The amount of neutralizing agents was expressed as molar ratio "r" or weight ratio "R" of Fe in evaluated AMD.

C. Method of transformation of Fe-products to ferrites spinel group of pigments [30]

Table 3 Characteristics of AMD solutions and content of the main heavy metal elements.

	pH	κ [mS·cm ⁻¹]	Concentration [mg·dm ⁻³]					
			SO ₄ ²⁻	Fe	Al	Zn	Mn	Cu
AMD1	2.45	8.59	13,260	2,420	656	5.9	45.5	< 0.03
AMD2	2.45	7.66	10,150	1,900	560	5.2	41.9	< 0.03

Other elements are present in minor quantities: Na, Si (1-4 mg·dm⁻³), K, Si (0.1-1.4 mg·dm⁻³), As (0.2-0.3 mg·dm⁻³), Cd, and Pb (5-30 µg·dm⁻³)

Individual components (Fe-precipitate, CaCO₃ and ZnO) were substantially homogenized in weight ratio correspondent to stoichiometric compounds of CaFe₂O₄, Zn_{0.2}Ca_{0.8}Fe₂O₄, and Zn_{0.4}Ca_{0.6}Fe₂O₄. Obtained pigments, after calcinations at 1050°C and 1095°C were ground in a globe mill for 4 hours, then washed with water and dried.

Results and Discussion

Recovery of Fe and Al Solid Products

Fe and Al in acid sulphate solution occur in the form of aqua-hydroxo-sulphate complexes. Solubility of these complexes, forms of exclusion (solid phase forms), and their properties (mainly specific surface and adsorption ability of Fe ochres) depend on many factors (pH, temperature, concentration of sulphates, time period, etc.). Neutralization of AMD at 20°C has a specific time behaviour with two inflex points (1st inflex at pH = 3.5 and value $r = 2.4$, 2nd inflex at pH = 5.5 and value $r = 4.03$), which corresponds with Fe³⁺ and Al³⁺ oxyhydroxide precipitation from solution (Fig. 1). Pure solid products can be obtained by precipitation with controlled values of pH and Fe or Al concentration in solution, respectively, without co-precipitation and adsorption of discrete components of AMD to precipitate (Table 4). The first product is created by schwertmanite on the base of sulphur content. In several forms Al can be precipitated from solution, e.g. basaluminite (Al₄(SO₄)(OH)_{10.5}(H₂O)), boehmite (γ -AlO(OH)), or alunite (KAl₃(SO₄)₂(OH)₆), respectively. Precipitation of other elements, mainly Mn, is less probable under these conditions.

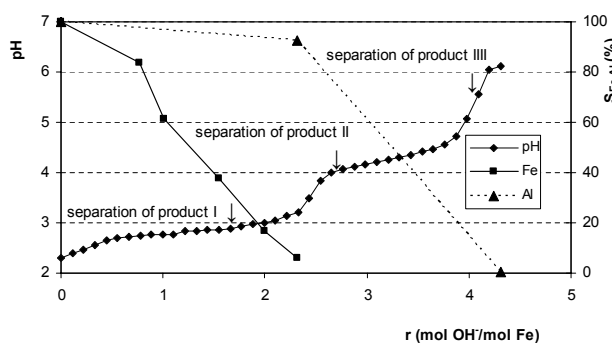


Fig. 1. Neutralization of AMD 1 by NaOH at 20°C ($S_{Fe,Al}$ – percent solubility of Fe and Al; I.-II.-III. – product from fraction precipitation denoted in Table 4).

Table 4. Product composition from neutralization of AMD1.

pH	Product	Content of main elements [%]			
		Fe	Al	Mn	S
Selective fractional precipitation					
3	I.	41.5	0.08	<0.01	3.8
4	II.	41.2	0.66	0.06	nd
5.2	III.	0.72	17.6	0.08	nd
Continuous precipitation					
6.9		29.8	9.3	0.28	5.2

Content of other elements (Zn, Cu, Co, Ni): 0.05%.

The Influence of Temperature during Neutralization of AMD on the Formation and Properties of Fe-ochres (abbrev. Fe-O)

The value of pH was increasing quite rapidly during the neutralization of AMD at laboratory temperature (20°C), with increasing doses of NaOH until the beginning of coagulation (at pH 2.8). There was almost no change in pH at 40°C and 60°C. At 90°C, pH dropped to 2.2 and remained at this level until the coagulation of Fe-O. There also is a difference in the beginning of coagulation (Fig. 2). These results suggest that temperature has a strong influence on the process of hydrolysis and the balance between colloid forms of Fe present in the tested AMD. A rapid decrease of pH at 90°C may be the result of Fe compound hydrolysis followed by elution of H₂SO₄ [31]. Increased temperature most likely destabilizes colloid soluble forms of Fe³⁺, which are consequently separated from the solution in the form of well-sedimenting aggregates. The same situation is found in the case of tested AMD. 60% of coagulate (most likely jarosite or eventually hydronium jarosite) was separated from the solution and solubility of Fe³⁺ decreased to the value 800 mg·dm⁻³ by heating AMD to 90°C.

The ochre precipitation of AMD is a simplification as different solid phases are formed at different pH, sulphate concentration, time, etc. Different forms of jarosite precipitate [(NaKH₃O⁺)Fe₃(SO₄)₂(OH)₆], schwertmannite [Fe₈O₈(OH)₆·SO₄·nH₂O], ferrihydrite (Fe₂O₃·1.8 H₂O or Fe(OH)₃), and goethite (α -FeOOH) are formed in the range pH 1.5-4.5 [20, 21]. Mixtures of different minerals are often

Table 5. Surface properties of Fe-O recovered from AMD at various temperatures.

Temperature [°C]	S_{BET} [m ² ·g ⁻¹]	V_A [cm ³ ·g ⁻¹]
20	23.4	0.058
40	114	0.134
60	192	0.242
90	215	0.252

observed, partly due to transformation processes into thermodynamically more stable minerals. Goethite is the most stable form that can be formed by transforming schwertmanite [32].

Temperature of precipitation markedly influenced the surface characteristics of Fe-O (Table 5). Specific surface area (S_{BET}) and total specific volume of pores (V_A) increase linearly as well as temperature of precipitation in the range of 20-60°C increases. Increasing specific volume of pores was markedly smaller at 90°C. Temperature of 60°C is sufficient for Fe-O production from AMD with specific surface area of about 200 m²·g⁻¹. Similarly, specific surface area also was observed by natural Fe-O [28]. Relationships between reaction and exacerbation temperature, phase constitution, and extent of specific surface area will be the subject of further research.

Treatment of AMD by the Use of Some Industrial Effluents (Immobilization of AMD Components by Waste from Industrial Processing)

Inhibition of AMD creation and its treatment described in literature was checked by using slime, RMB, and BFS. It is necessary to use these materials in the form of fine powder, especially under laboratory conditions. In the case of coarse particles it is covered by formed precipitate and, furthermore, it is ineffective. Changes of pH values, concentration of Fe and SO₄²⁻ in solution during the addition of tested agents and composition of mother liquor after treatment of AMD by using of CaCO₃, RMB, and BFS are shown in Fig. 3 and Table 6.

Differences in the stage of Fe and Al precipitation within the frame of tested agents were negligible and residual concentrations of these elements in the mother liquor did not exceed quality limits in the surface water. More distinctive changes were observed by decreasing of manganese concentration in the mother liquor. A large amount of Fe-O in original and in created product can induce almost quantitative elimination of manganese with treatment of AMD by RMB. Concentration of Mn was decreased to 22% and 60% by the treatment of AMD with slime or RMB, respectively. Elimination of As below 0.005 mg·dm⁻³ can probably be considered as a result of adsorption on formed Fe-O [33]. Binding of As⁵⁺ on schwertmanite also can inhibit its transformation to stable goethite [34].

Sulphate decreasing as a result of the formation of low-soluble gypsum depends on availability of Ca²⁺, i.e. Ca²⁺ released from agents matrix in AMD surrounding. Concentration of SO₄²⁻ decreased almost linearly with the addition of slime to AMD up to pH value was about 5.5. Further addition of slime was inefficient, which is related to low solubility of slime at higher pH values. It means that materials with Ca contents can only partially decrease sulphate concentration. In the case of slime, sulphate concentration decreased to the value of about 3.5 g·dm⁻³ (about 30% decrease from original value in AMD) and in the case of RMB or BFS to the value of about 5.3 g·dm⁻³, respectively (about 43% decrease from original value in AMD). Similar yields concerning the decrease of sulphate concentration in AMD treatment by whitewash are described in a paper by Maree et al. [35]. For further sulphate-concentration decrease in AMD below limit values for surface water a treatment with another method is required, e.g. precipitation with Ba²⁺ or anaerobic purification with sulphate reducing micro flora [10]. Variation of neutralization agents consumption correlated with content of alkalinity carrier in the order CaCO₃<BFS<RMB. Products of this neutralization can serve as components of construct materials, e.g. cement composites described in [36], where 10% of sludge from AMD treatment was combined with slime, 2.5% Portland cement, and 87.5% fly ash from coal incineration to produce low-strength composites.

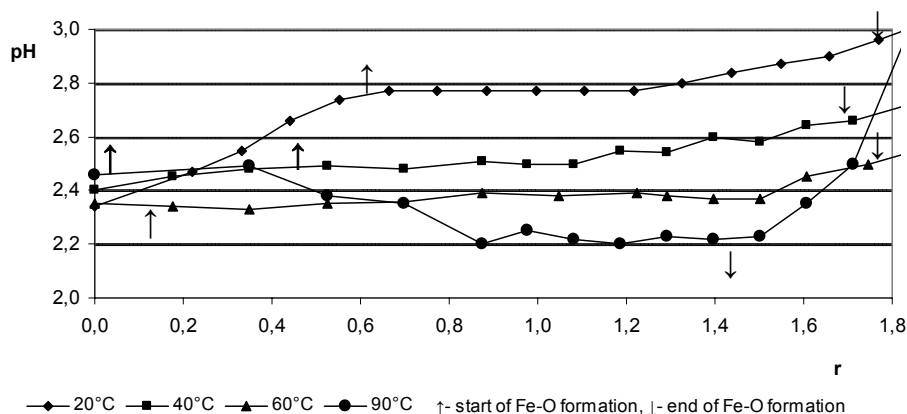


Fig. 2. Variation of pH values during the addition of NaOH at 20, 40, 60, and 90°C.

Table 6. Characteristics of mother liquor after AMD treatment using CaCO_3 , RMB, and BFS.

Parameter	Act No. 296/2005 Coll.*	Treating agent/dose**		
		$\text{CaCO}_3/16$ *(AMD 2)	RMB/50 *(AMD 2)	BFS/21 *(AMD 1)
pH	6-8.5	6.7	6.9	6.8
κ [$\text{mS}\cdot\text{cm}^{-1}$]		3.5	3.9	5.87
Sulphate [$\text{mg}\cdot\text{dm}^{-3}$]	250	3300	5220	5570
Concentration [$\text{mg}\cdot\text{dm}^{-3}$]				
Fe	2	< 0.1	0.1	< 0.1
Al	0.200	0.15	0.200	0.26
Mn	0.300	9.66	0.24	40
Ca	200	561	530	530
Mg	100	359	260	998
As	0.030	< 0.005	< 0.005	< 0.005
Zn	0.100	0.016	0.01	0.17
Cu	0.020	0.035	0.012	0.02
Co	0.050	0.035	0.002	
Cr	0.100	< 0.005	0.21	< 0.005
Ni	0.020	0.009		0.096

*Act No. 296/2005 Coll. – on surface water quality

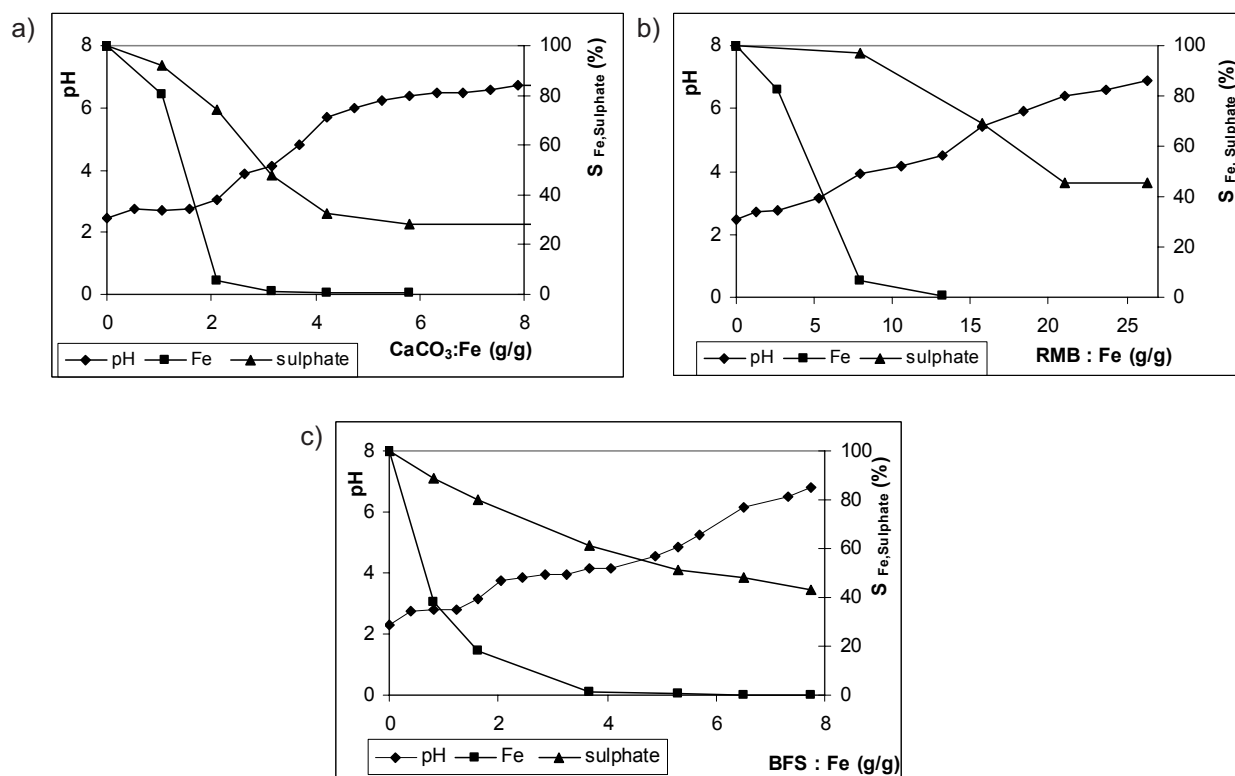
**Dose – agents consumption in $\text{g}\cdot\text{dm}^{-3}$ of AMDFig. 3. Variation of pH values, Fe, and sulphate concentrations in solution during the addition of neutralization agents a) CaCO_3 , b) RMB, and c) BFS.

Table 7. Ferric sludge weight loss during calcinations at different temperatures for a 4 hour-period.

Temperature [°C]	200	400	600	800	1000
Δm [%]	21.7	26.6	36.5	41.2	41.6

Δm [%] – weight loss (mean value from 2 parallel test runs)

Table 8. Characteristics of synthesized ferrite-type pigments.

Wanted compound	Phase composition		
	Structure – mineral	Crystallographic systems	Content [%]
	Temperature calcination: 1050°C		
$Zn_{0.4}Ca_{0.6}Fe_2O_4$	Fe_2O_3 – hematite	<i>Rhombohedral</i>	32
	ZnFe₂O₄ – zincferrite	Cubic	23
	$Ca_2Fe_{15.588}O_{25}$	Hexagonal	25
	$Ca_2Fe_{15.51}O_{25}$	Rhombohedral	20
$Zn_{0.2}Ca_{0.8}Fe_2O_4$	Fe_2O_3 – hematite	<i>Rhombohedral</i>	49
	ZnFe₂O₄ – zincferrite	Cubic	12
	Fe₂CaO₄ – calciumferrite	Orthorhombic	20
	$Ca_2Fe_{15.6}O_{25}$	Hexagonal	19
$CaFe_2O_4$	$Ca_2Fe_{15.6}O_{25}$	Hexagonal	19
	Fe_2O_3	<i>Rhombohedral</i>	50
	CaFe₂O₄	Orthorhombic	32
	$Fe_2O_3(CaO)_2$	Orthorhombic	18
Temperature calcination: 1095°C			
$Zn_{0.4}Ca_{0.6}Fe_2O_4$	Fe_2O_3 – hematite	<i>Rhombohedral</i>	22
	ZnFe₂O₄ – zincferrite	Cubic	50
	$Ca_2Fe_2O_5$	Orthorhombic	12
$Zn_{0.2}Ca_{0.8}Fe_2O_4$	Fe_2O_3 – hematite	<i>Rhombohedral</i>	25
	ZnFe₂O₄ – zincferrite	Cubic	22
	Fe₂CaO₄ – calciumferrite	Orthorhombic	53
$CaFe_2O_4$	Fe_2O_3	<i>Rhombohedral</i>	23
	CaFe₂O₄	Orthorhombic	67
	$CaFeSi_2O_6$	Orthorhombic	10

Transformation of Ferric Sludge/Precipitate to Pigments

Solid polymorph forms of Fe-O, such as products isolated from AMD, undergo a process of dehydration and dehydroxylation under the influence of increased temperature. Dehydroxylation of Fe-forms occurs in the broad temperature range of 140-500°C, depending on the nature of involved chemical compounds, crystalline structure, and the range of isomorph substitution [32]. Final product of dehydroxylation is hematite, besides the intermediate phase

of lepidocrocite and maghemite. Weight loss during calcination at temperatures of 200, 400, 600, 800, and 1000°C during the 4-hour period showed that at temperatures above 600°C there is no significant change of weight. Thus we could assume that there is no further dehydration and dehydroxylation and that hematite was formed (Table 7). Each thermal stress resulted in forming a different colour tone (from brown to violet).

Ferrites originate from metal oxides, carbonates, or hydroxides via reaction of metal in the solid phase. In aerobic surrounding at about 1000°C, the oxygen grid is

formed, through which penetrate cations of metals. Generated spinel structures have anticorrosive properties and they are stable up to 1,300-1,400°C [37, 38].

Experimental results from synthesis of ferrite structures represented with cubic and orthorhombic crystallographic systems imply that temperature of calcification is a significant factor (Table 8). Cubic structures generated at calcinations temperature of 1,095°C and responding to zincferrite is about double more frequented as in the case of products generated at 1,050°C. Hematite phase formed a high-level part (32-46%) in all tested pigments. Each of prepared pigments was brown and extra hard, which can induce complications during their dispergation in coating composition.

All this information suggests that reactions in solid phase are complex processes, resulting in the formation of several phases. Each of these pigments may contribute to anticorrosive properties of the painting coat in a different way.

Conclusion

This paper presents various possibilities of AMD treatment to Fe-O (Fe-hydroxides and Fe-oxides) with useful properties (e.g. as adsorbent, entrance raw materials for pigments, etc.) and remediation possibilities (immobilization of main contaminant bioavailability) by the use of various industrial effluents. Ferric and aluminium hydroxides can be recovered from the tested AMD without co-precipitation of other components with the yield of above 90% (yield of Fe-O = 92.6±4.0) by convenient selection of conditions and by process control during the sequential precipitation mainly with monitoring of Fe and Al solubility, respectively. Fe-O particles with specific surface area of about 200 m²·g⁻¹ are formed in AMD at higher temperatures (above 60°C).

Calcinations at 600-800°C produce not only ferric sludge, but also Fe and Al mixed products from AMD, which are finished by dehydration and dehydroxylation processes related to creation of the main phase of hematite. This phase presents the platform of commercial ferric pigments, e.g. Fepren [39]. The additional possibility of ferric sludge utilization in the scope of pigments with anticorrosive impact is the synthesis of ferrites as the main component, e.g. zincferrite.

Treatment of AMD by the use of industrial effluents containing Ca (e.g. red mud bauxite, blast furnace slag, and slime) results in almost quantitative elimination of Fe, Al, and As. The content of minority elements (Mn, Zn, Cu, etc.) is markedly reduced as a result of precipitation or by adsorption to formed sludge. Sulphate reduction in the gypsum form also was significant, from an original concentration of 10.1 and 13.3 g·dm⁻³ it decreased to 2.2 and 5.5 g·dm⁻³, respectively (level of removing is 72 or 55%, respectively).

Acknowledgements

This work was supported by Slovak-Czech Intergovernmental Scientific-Technical Cooperation (APVV SK-CZ-0139-11) by a grant from the Ministry of

Education of the Slovak Republic KEGA No. 011TUZVO-4/2011, and by the Ministry of Education, Youth, and Sports of the Czech Republic (Project No. 7AMB12SK155).

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