

REFINED COAGULANT FOR WATER PURIFICATION FROM ESTONIAN GLAUCONITE

I. DIGESTING GLAUCONITE WITH SULPHURIC ACID IN SLURRIES

Rein KUUSIK, Ludmilla VIISIMAA, and Ernst AASAMÄE

Tallinna Tehnikaülikool (Tallinn Technical University), Ehitajate tee 5, EE-0026 Tallinn, Eesti (Estonia)

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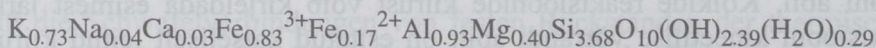
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Abstract. The process of obtaining refined Al-Fe coagulants from Estonian glauconite was investigated. The raw material (preferably washed ore) was digested with sulphuric acid, the resulting slurries were neutralized and filtered to separate the insoluble residue. Kola nepheline and oil shale ashes were recommended as neutralizing reagents. Liquid or solid coagulants were produced.

Key words: glauconite, sulphuric acid treatment, filtration, neutralization, coagulants.

INTRODUCTION

Glauconite is a wide-spread mineral, green in colour, which belongs to the hydrous mica group. In Estonia glauconite is found in the Lower Ordovician sediments in the form of round pellets blended with sandstone. The highest-grade glauconite-bearing stratum lies at depths from 5 to 190 m and has an average thickness of 1 m [1–3]. On the basis of statistically found coefficients [4] the chemical composition of the typical Estonian glauconite may be expressed by the following formula:



Enrichment of glauconite ore by washing off fine particles of clay minerals, followed by magnetic separation of glauconite from quartz, has been studied by Vilbok [5] and Silver & Ahelik [6]. Possibilities of using

glaucanite for the production of pigments, water softening reagents, coloured building materials, and potassium fertilizers have been discussed in earlier works [5, 7–9]. At the present time Estonian glauconite deposits are not exploited.

Sulphuric acid digestion of Estonian glauconite was first investigated with the aim of obtaining potassium fertilizers and iron, aluminium, and magnesium salts. It was found that a prolonged mixing time (about 4 h), rather high temperature (110–120°C), and an excess of sulphuric acid as compared to the theoretical requirement, must be used [9].

Sulphuric acid treatment of glauconite in order to produce coagulants for water purification has been studied at Tallinn Technical University (TTU). In our first research project the suitability of glauconite for obtaining a coagulant by the so-called den process was tested. The den process technology includes a rapid mixing of the reagents and prolonged denning of the resulting slurry in a superphosphate den with a resultant formation of a solid coagulant [10]. Our investigations show that Estonian glauconite may be used as a raw material for producing coagulants which contain approximately 12% of active elements (sum of Al_2O_3 and Fe_2O_3 in terms of Al_2O_3) and it may be used in the water purification process with the same efficiency as the coagulants obtained from nepheline [10].

The aim of our subsequent studies on the same subject was to increase the content of active elements in coagulants by removing the insoluble residue. This residue consists mainly of silicic acid and may be eliminated by two methods:

- filtrating the slurry immediately after the digestion of glauconite; and
- solving the coagulant obtained by the den technology in water, with the following filtration.

In this paper the former method is discussed, as it is preferable both from the technological and the economical point of view.

It is known that, unlike the den process, the filtration of the slurry requires long-time mixing of the reagents to provide a sufficiently high degree of solubility of the active elements. Therefore, accelerating the digestion of glauconite must be regarded as the prime task. As established in the earlier works, increasing the concentration and quantity of the acid and raising the temperature of the slurry may be used for that purpose. However, a great quantity of acid brings about a need for the neutralization of the resulting slurries.

Another precondition for a successful realization of the process discussed is a sufficiently high filtration rate of the insoluble residue. The slurries obtained by digesting silicate minerals with sulphuric acid have been found, as a rule, to filtrate quite slowly due to the presence of amorphous silicic acid and tiny particles of accompanying minerals [11]. To accelerate filtration certain flocculants, mostly derivatives of polyacrylamide, are used [11].

In view of the above information, the present work was carried out in three parts:

- (1) research into the kinetics of digesting glauconite with the aim of defining a proper technology for gaining high degrees of the solubility of active elements;
- (2) experiments of digesting various samples of glauconite in order to determine the need for the enrichment of the raw material;
- (3) research into neutralization and filtration of the reaction slurries to find out the most suitable reagent for the process.

The characteristics of the coagulants obtained in the course of the present work as well as the composition and utilization potentials of the separated solid wastes will be discussed in another paper.

EXPERIMENTAL

In this work four samples of Estonian glauconite were used (Table 1):

- (1) primary ore of glauconitic sandstone, gently ground in a ball mill;
- (2) washed ore obtained from sample 1 by rinsing out small clay particles;
- (3) primary concentrate obtained from sample 2 by magnetic separation;
- (4) ground concentrate obtained from sample 3 by grinding the latter in a disintegrator mill.

The chemical composition and particle size of the samples were determined in the laboratories of TTU and the Geological Survey of Estonia by standard methods.

The characteristics of the samples (Table 1) show that combined enrichment of glauconitic sandstone resulted in a 4% increase in the content of iron and a 5% increase in the content of SiO_2 . A significantly smaller increase in the content of aluminium, potassium, and magnesium was noted. The composition of samples 1–4 is almost the same as that of the specimens analysed in the earlier works [10]. The data of Table 1 indicate that in samples 1–3 the major part of the particles (93–98%) are of a size 0.05–0.63 mm, while in sample 4 this fraction makes up only 52%.

Using the chemical composition of the samples the theoretical requirement of sulphuric acid for their full digestion was calculated. The content of the four main components of glauconite (iron, aluminium, potassium, and magnesium) was taken into account in the calculations.

In the first stage of the experiments all four samples of glauconite were used. The technological parameters varied in the following range:

- concentration of sulphuric acid from 30 to 70% H_2SO_4 ;
- quantity of sulphuric acid from 80 to 150% as compared to the theoretical requirement;
- temperature in the reactor from 105 to 135°C;
- time of mixing from 5 to 180 min.

Table 1

Characteristics of glauconite, %

Sample	Chemical composition ^a						Particle size, mm			
	SiO ₂ , tof ^b	Fe ₂ O ₃ , tof ^b	Al ₂ O ₃	K ₂ O	MgO	+0.63	+0.18 -0.63	+0.05 -0.18	-0.05	
1. Primary ore	56.3	16.3	7.7	6.7	2.7	1	71	27	1	
2. Washed ore	54.8	17.6	8.3	6.7	2.9	3	57	36	4	
3. Primary concentrate	51.5	20.2	8.7	7.9	3.3	1	71	25	3	
4. Ground concentrate	51.1	20.2	8.8	7.9	3.2	0	0	52	48	

^a Samples contained also 2.4-2.7% FeO, 1.5-2.4% CaO, and 1.6-2.1% CO₂.

^b Sum of SiO₂ from glauconite, other silicate minerals, and quartz.

^c Sum of all compounds of iron expressed in terms of Fe₂O₃.

In the following stages of our work the technological parameters of the process were chosen on the basis of the results of the first series of the experiments.

Glaucanite digesting was carried out at a controlled temperature in a porcelain reactor with a capacity of 275 cm³. The digester was equipped with a mechanical stirrer, a reflux flow condenser, and a heating bath. The initial sample of glaucanite (20–50 g) was added to the heated sulphuric acid solution, after which the mixing continued within a fixed time. During the treatment of glaucanite in the digester, samples of slurry were taken for determining the solubility of the active elements. These samples were immediately watered down in weight ratio 1:10 to disrupt the reaction of glaucanite digestion. The diluted samples were filtrated and the filtrates analysed.

In the second and third stages of this work a flocculant (N-300, prepared by Kemira, Finland) was dosed into the digester 2 min before the end of the mixing, in an amount of 0.0025% from the weight of the reagents. The resulting slurry was diluted with water in the weight ratio 1:0.5 or 1:1 and filtrated at 90°C, using a suction filter and a Lavsan (polyester fabric) filter cloth. The filtration was carried out at the vacuum of 40 kPa, measuring the filtration rate in terms of the volume of the filtrate in 1 m³ per 1 m² of the filtering area per hour. The filter cake was washed up to neutral reaction and dried at 105°C. The solid obtained and the primary filtrate (product solution) were analysed by ordinary methods.

In the third stage of the present investigation four reagents were tested for the neutralization of acidic slurries: (1) lime, (2) limestone, (3) ashes of oil shale, and (4) nepheline concentrate. The requirement of reagents 1–3 was calculated on the basis of their CaO content, but in the experiments with nepheline the content of Fe₂O₃, Al₂O₃, Na₂O, and K₂O in the raw material was considered as well. Neutralizing additives were dosed into the digester after the flocculant and water had been added. The resulting slurry was mixed for another 5–10 min and filtrated as described above. In the experiments with limestone neutralization was carried out in another larger vessel because of intensive foaming.

When nepheline was used, an additional technological method was tested, by which the reaction slurry from glaucanite digesting was filtered after diluting. Nepheline was added to the filtrate. The resulting mixture, having a porridge-like consistence, could be processed to a solid coagulant.

RESULTS AND DISCUSSION

Kinetics of glaucanite digesting with sulphuric acid

Typical curves of digesting various samples of glaucanite are quite similar in appearance (Figs. 1–3). In all the experiments higher degrees of the solution of aluminium as compared to iron were observed. The

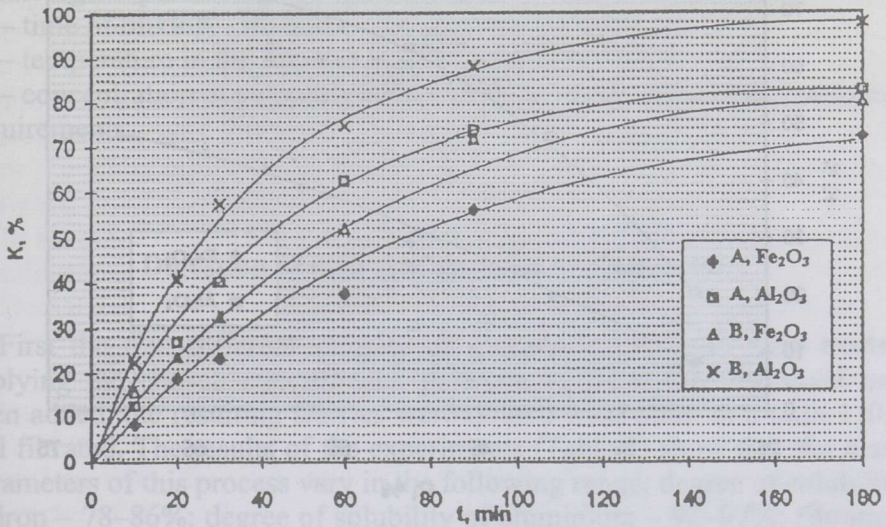


Fig. 1. The effect of the quantity of sulphuric acid and the processing time (t) on the solubility degree of iron and aluminium (K) for washed glauconite ore digested in 40% H_2SO_4 at 120°C. Quantity of the acid: A 100%, B 150% of the theoretical requirement.

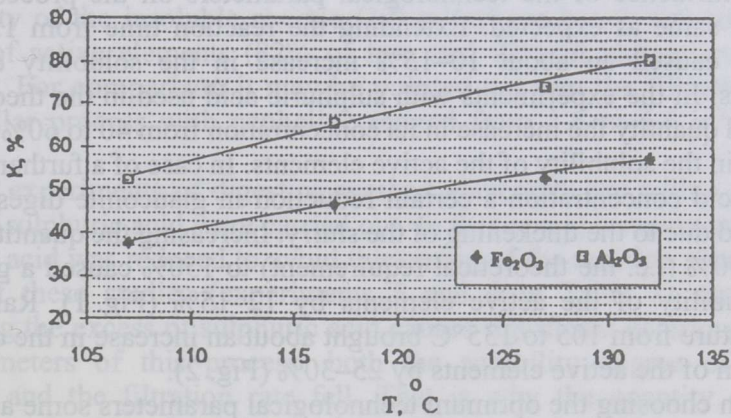


Fig. 2. The effect of the processing temperature (T) on the solubility degree of iron and aluminium (K) for primary glauconite ore digested during 30 min in 60% H_2SO_4 (quantity 150% of the theoretical requirement).

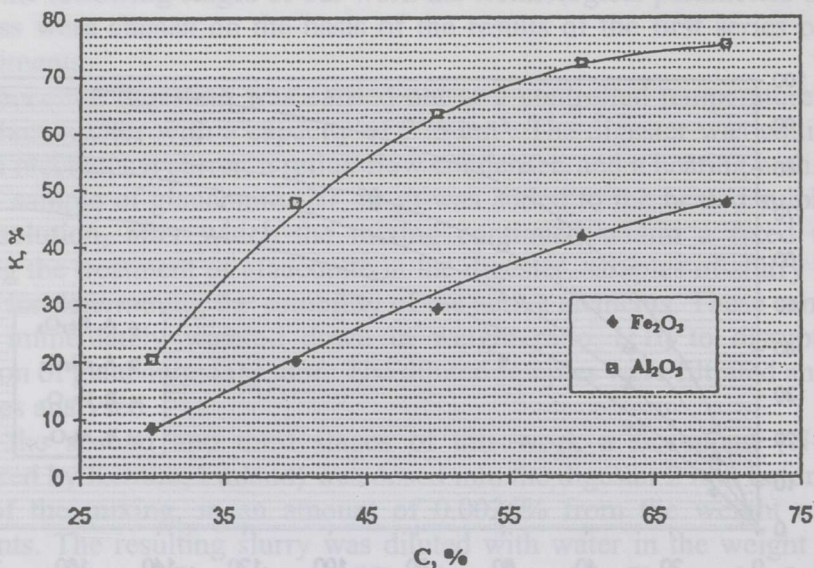


Fig. 3. The effect of the acid concentration (C) on the solubility degree of iron and aluminium (K) for primary glauconite concentrate digested during 30 min at 120°C. Quantity of H₂SO₄ 100% of the theoretical requirement.

difference was as high as 15–30%. Poor solution of iron may be due to the peculiarities of glauconite structure [12] and also the hydrolysis of ferrous sulphates with precipitation of such salts as Fe(OH)SO₄ or K₂[Fe₆(SO₄)₄(OH)₁₂] [11].

The influence of the technological parameters on the process results was the same as expected. Extending the reaction time from 1.5 to 3 h (Fig. 1) caused an about 10–15% increase in the solubility of active elements. In the experiments with sulphuric acid used in the theoretically required quantity the increase in its concentration from 40 to 60% caused a growth in the solubility of the active elements. In case of a further increase in the acid concentration a certain reduction in glauconite digesting was observed due to the thickening of the slurry. Increasing the quantity of acid from 100% (i.e. the theoretical requirement) to 150% caused a growth in the solubility of the active elements by 12–15% (Fig. 1). Raising the temperature from 105 to 135°C brought about an increase in the degree of digestion of the active elements by 25–30% (Fig. 2).

When choosing the optimum technological parameters some additional constraints must be taken into consideration:

- prolonged mixing causes a drop in the productivity of the equipment;
- high temperature induces intense corrosion of the apparatus;
- high concentration of sulphuric acid causes a deterioration of the flowability of the slurry;
- large excess of acid brings forth the necessity of using considerable amounts of neutralizing additives.

On the basis of a critical analysis of the data on the kinetics of the present process and the constraints mentioned, the following basic technological parameters were established for further experiments:

- time of mixing – 90 min;
- temperature in the digester – 130°C;
- concentration of sulphuric acid – 150% as compared to the theoretical requirements.

Digestion of different samples of glauconite

First the four different samples of glauconite (Table 1) were treated applying the chosen experimental parameters. After the flocculant had been added, the resulting slurries were diluted with water in a ratio 1:0.5 and filtrated. The results of the experiments (Table 2) show that the main parameters of this process vary in the following range: degree of solubility of iron – 78–86%; degree of solubility of aluminium – 92–97%; filtration rate – 0.2–1.9 m³/m² per hour. From the accessory elements magnesium was solved up to 90–100%, and potassium 87–90%.

The data in Table 2 show that washing off clay particles from the glauconite ore brought about a significant increase in the filtration rate, from 0.7 to 1.9 m³/m² per hour, and a slight improvement in the solubility of iron (experiments 1 and 2). In the experiments of digesting glauconite concentrates the highest solubility degrees of active elements were attained, but the filtration rate was extremely low (0.2–0.4 m³/m² per hour). Therefore, washed glauconite ore should be regarded as the most suitable raw material for this process, since, in addition to a good filterability of the insoluble residue (1.9 m³/m² per hour), fair solubility degrees of active elements (82% of iron and 92% of aluminium) were achieved. For comparison it may be pointed out that the filtration rate of a similar process with nepheline ranged from 1.6 to 4.6 m³/m² per hour [11].

A few experiments of digesting washed glauconite ore with a smaller excess of sulphuric acid were carried out. In that case the concentration of sulphuric acid was reduced to avoid thickening of the reaction slurry. The results of these studies (experiments 5 and 6 in Table 2) show that decreasing the excess of sulphuric acid causes significant deterioration of the parameters of this process: both the solubility degree of active elements and the filtration rate fell. That is why the quantity of acid amounting to 150% of the theoretical requirement should be regarded as optimum. However, in that case about 38% of the sulphuric acid remains unused in the product filtrate. In coagulants the content of free acid should not exceed 0.1% [13, 14]. For that reason the filtrates from digesting glauconite (Table 2) need to be neutralized.

Table 2

Digesting various glauconite samples^a (2nd part of the experiments)

Experiment	Sample of glauconite	Sulphuric acid		Composition of the diluted filtrate ^b			Solubility degree, %		Filtration rate, m ³ /m ² per hour
		Concentration, % H ₂ SO ₄	Quantity, % of theoretical requirement	Fe ₂ O ₃	Al ₂ O ₃	Free H ₂ SO ₄	Fe ₂ O ₃	Al ₂ O ₃	
1.	Primary ore (1)	60	150	4.5	2.5	13.4	78	91	0.7
2.	Washed ore (2)	60	150	5	2.7	11.4	82	92	1.9
3.	Primary concentrate (3)	60	150	5.5	2.7	10.6	83	95	0.4
4.	Ground concentrate (4)	60	150	5.8	2.8	10.8	86	96	0.2
5.	Washed ore (2)	50	120	4	2.4	8.1	70	85	1.3
6.	Washed ore (2)	40	100	3.8	2.2	6.8	56	73	0.8

^a Mixing time 90 min, temperature 130°C.

^b The filtrates contained 1.6–2.3% K₂O and 0.8–1.0% MgO.

Neutralizing the reaction slurries

Experiments of neutralizing the slurries obtained by digesting washed glauconite ore (Table 3) show that all four additives may be regarded as equal with respect to their neutralizing capability. The content of free acid in the product filtrate after neutralization was up to 0.1% (Table 3). Therefore, the second main criterion in this process – the filtration rate – must be considered when choosing the most suitable neutralization additive.

In all cases the addition of a neutralizing additive caused a significant deterioration of the filterability of the solid phase. The filtration rate for the initial acidic filtrate was $1.9 \text{ m}^3/\text{m}^2$ per hour (Table 2, experiment 2), but for the neutralized ones only $0.1\text{--}0.2 \text{ m}^3/\text{m}^2$ per hour. The highest value was attained in the experiment in which ashes of oil shale were used. It must be noted that the filtration rate could be significantly increased by increasing the water:slurry ratio and by adding a bigger amount of the flocculant into the reactor. At the values of the above-mentioned parameters 1:1 and 0.005%, respectively, the filtration rate increased up to $0.9\text{--}1.4 \text{ m}^3/\text{m}^2$ per hour.

Being an industrial waste oil shale ash is also the cheapest among the reagents used, therefore preference should be given to its use. Limestone is another cheap reagent, but because of its intensive foaming it may cause certain inconvenience.

The method of using nepheline as a neutralizing additive may be regarded as a two-stage process for obtaining coagulants from two different raw materials. In the first stage glauconite, a poorly solving material, is treated with excessive sulphuric acid. In the second stage a readily solving mineral, nepheline, is added to neutralize the free acid. This is how a high degree of using both the acid and the mineral raw materials is achieved and the content of aluminium in the product increases by about 50% (relative) as compared with using only glauconite. As in this process the adding of nepheline causes a significant thickening of the product slurry, it is advisable to separate the insoluble residue after the first stage of the process, to neutralize the filtrate, and to produce a solid coagulant after the evaporation of the neutralized mixture.

Potential technological solutions

On the basis of the results of this work three different methods for obtaining refined coagulants from Estonian glauconite may be suggested (Fig. 4). All of them are based on a prolonged mixing of glauconite with sulphuric acid taken in excess, followed by separation of the insoluble residue. According to method (a) a large quantity of sulphuric acid (150% as compared to the theoretical requirement) is used. The product filtrate is neutralized with nepheline and the neutralized mixture evaporated, thus a solid coagulant is obtained. In case of method (b) a smaller quantity of

Table 3

Results of neutralizing the obtained slurries by digesting washed glauconite ore

Supplement	Neutralizing supplement			Chemical composition, %				Composition of neutralized solutions, %				Filtration rate, m^3/m^2 per hour
	Quantity per 1 g of H_2SO_4 , g	Content of particles 0.1 mm, %	CaO	Fe ₂ O ₃ tot			Free H ₂ SO ₄	Fe ₂ O ₃	Al ₂ O ₃	Al ₂ O ₃		
				Fe ₂ O ₃ tot	Al ₂ O ₃	Al ₂ O ₃						
1. Lime	0.57	14	85	-	-	-	0	4.7	2.4	0.11		
2. Limestone	1.46	19	39.3	1.8	-	-	0.02	4.8	2.4	0.14		
3. Ashes of oil shale	1.16	45	49.1	5.7	4.9	-	0	5	2.9	0.22		
4. Nepheline concentrate*	0.96	62	1.5	3	28.5	-	0.08	4.9	6	0.09		

* Nepheline contained also 14% Na₂O and 7% K₂O.

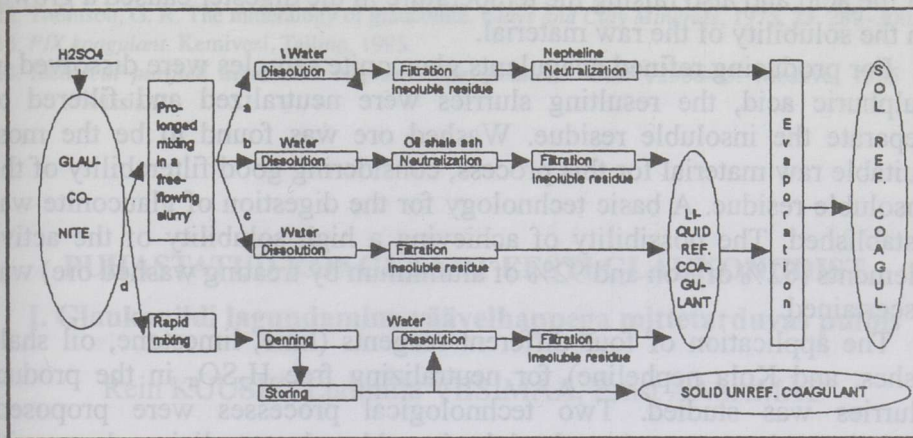


Fig. 4. Technological scheme for obtaining refined coagulants from Estonian glauconite. For method (d) the use of glauconite-nepheline mixture is recommended.

sulphuric acid (120%) is used and the product pulp is neutralized with ashes of oil shale. After that filtration follows. The end filtrate may be used as a liquid coagulant or be processed to a solid product. Method (c) is characterized by digesting glauconite with using sulphuric acid near the theoretically required quantity (80–100%). Liquid or solid coagulants may be obtained without any addition of neutralizing materials, but the product could contain up to 4.5% of free acid. Because of the high solubility degree of the raw materials and the highest quality of coagulants obtained, method (a) should be regarded as optimum.

Method (d), which has not been studied in this work, involves dissolving a solid coagulant obtained by the den process in a large amount of water, with the following separation of the insoluble residue. As compared to methods (a), (b), and (c), the last one seems to be the least convenient both from the technological and the economical point of view.

In all the above methods the most complicated stage of the process is the separation of the insoluble residue, due to its low filterability.

CONCLUSIONS

A laboratory study was conducted to elaborate methods for obtaining refined Al-Fe coagulants from Estonian glauconite. The chemical composition of four different samples of glauconite (primary and washed ore, primary and ground concentrate) was established. The kinetics of the digestion of the above samples by sulphuric acid in free-flowing slurries

was investigated. It was found that increasing the concentration or quantity of the acid and also raising the temperature in the digester caused a growth in the solubility of the raw material.

For producing refined coagulants glauconite samples were dissolved in sulphuric acid, the resulting slurries were neutralized and filtered to separate the insoluble residue. Washed ore was found to be the most suitable raw material for this process, considering good filterability of the insoluble residue. A basic technology for the digestion of glauconite was established. The possibility of achieving a high solubility of the active elements (82% of iron and 92% of aluminium by treating washed ore) was ascertained.

The application of four different reagents (lime, limestone, oil shale ashes, and Kola nepheline) for neutralizing free H_2SO_4 in the product slurries was studied. Two technological processes were proposed: (a) using a large quantity of sulphuric acid and neutralizing slurry with nepheline; and (b) using a smaller excess of acid and neutralizing slurry with oil shale ashes.

By process (a) a solid coagulant is produced, by process (b) either liquid or solid products may be obtained. Preference should be given to process (a).

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PUHASTATUD KOAGULANT EESTI GLAUKONIIDIST

I. Glaukoniidi lagundamine väävelhappega mittetarduvas pulbis

Rein KUUSIK, Ludmilla VIISIMAA, Ernst AASAMÄE

On näidatud võimalusi vedela või tahke puhastatud Al–Fe-koagulandi saamiseks glaukoniitliivast. On välja töötatud protsessi põhistaadiumide (lagundamine, neutraliseerimine, filtrimine) läbiviimise tingimused ning leitud sobivaimad lisandid (nefeliinikontsentraat, põlevkivituhk) happeliia neutraliseerimiseks.