Proc. Estonian Acad. Sci. Chem., 1996, **45**, 1/2, 56–69
https://doi.org/10.3176/chem.1996.1/2.06

REFINED COAGULANT FOR WATER PURIFICATION FROM ESTONIAN GLAUCONITE

II. CHARACTERISTICS OF THE PRODUCTS AND SOLID WASTES

Ludmilla VIISIMAA, Rein KUUSIK, and Ernst AASAMÄE

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

Presented by R. Munter

Received 28 March 1996, accepted 3 June 1996

Abstract. Composition, properties, and use of refined Al–Fe coagulants were investigated. Liquid coagulants contained about 5% of active elements in terms of Al_2O_3, solid ones from 15 to 16%. The best results in the water purification process were achieved with solid coagulants. The content of heavy and toxic microelements in the purified water did not exceed the maximum permissible level. The solid waste (glaucosil) proved to be a proper adsorbent for removing PO_4^{3-} ions from waste water. It could be also recommended as a component for the production of expanding concretes.

Key words: glauconite, Al–Fe coagulants, water purification, heavy metals, toxic elements, solid waste, PO_4^{3-} adsorption.

INTRODUCTION

In our previous paper the possibility of obtaining refined Al–Fe coagulants by sulphuric acid treatment of Estonian glauconite was shown. Several methods for the realization of the process, varying in the conditions of glauconite digestion, in the kinds of neutralizing additives, as well as in the succession of the stages of neutralization and filtration, have been worked out [1].

The coagulants used for the purification of water from suspended impurities and colloids differ from one another in the kind and valency of the main active element, the pH, the physico-chemical properties (solid, fluid, unrefined, refined), and the field of application (for purification of drinking water, treatment of industrial waste water or municipal sewage, precipitation of certain elements). The coagulating ability of the reagents

results from the hydrolysis of some of their specific ingredients. Depending on the surface properties, the rate of adsorption or adhesion of the impurities and, accordingly, the efficiency of coagulants may vary.

In water purification practice salts of aluminium or iron (sometimes their mixtures, the so-called dual or mixed coagulants) are usually used, with the weight ratio of Al_2O_3 to Fe_2O_3 varying from 1:0.5 to 1:3. The dual coagulants may be added to water either separately or in the form of mixtures. The latter case ought to be preferred because of simpler dosage [2]. The coagulation mechanism in case of using dual coagulants is complicated and insufficiently explored. The comparative data on the efficiency of dual and single coagulants are contradictory. As declared in [2], mixed coagulants may be used in a larger range of pH values, the particles of hydroxides precipitate more uniformly and a higher degree of water clarification is achieved. Other authors [3] have found that combining Al and Fe coagulants does not result in a more effective coagulation.

Coagulants obtained from glauconite contain aluminium and iron sulphates as active elements (AE) and differ in their composition from the mixed coagulants presented in literature [2, 3]. This difference may have an effect on their hydrolysis and coagulating activity.

In the process of obtaining a refined coagulant from glauconite solid wastes (i.e. insoluble residue) are formed in addition to the products. The quantity of wastes is as high as 0.7–1.1 g per 1 g of glauconite. As shown by Anso [4] these wastes (so-called glaucosil) consist mainly of amorphous SiO_2 mixed with a smaller amount of quartz and other minerals insoluble in sulphuric acid. The possibility of using glaucosil as a cleaning powder, for the adsorbtion of vapours of organic compounds, and for the stabilization of soil has been suggested [5]. The siliceous wastes from the processes of producing Al coagulants (so-called Si-stoff) have a similar composition. The possibility of utilizing them as a raw material for producing cement, glass, and ceramics, and as an additive to the gypsum binder or a porous filling material for light concrete has been proved [6].

In this work the results of an investigation of the composition and properties of mixed coagulants obtained from glauconite are presented. The distribution of microelements in the processes of producing and utilizing coagulants and the composition of solid wastes and the possibility of using them are discussed.

EXPERIMENTAL

Four samples of refined coagulants obtained from Estonian glauconitic sandstone were used as objects for this investigation. The glauconitic raw material contained 54.8% SiO_2, 17.6% Fe_2O_3, 8.3% Al_2O_3, 6.7% K_2O, and 2.9% MgO. The experimental methods for obtaining the above coagulant samples are presented in the first part of the present work [1].

The samples of coagulants 1–4 (Table 1) represent products of various technological methods differing mainly in the quantity of sulphuric acid

Table 1

Characteristics of the samples

Parameters	Liquid coagulants		Solid coagulants	
	1	2	3	4
1. Conditions of glauconite digestion:				
– quantity of H_2SO_4, % of theor. requirement	100	120	120	150
– concentration of acid, %	40	50	50	60
– temperature, °C	120	130	130	135
– time, min	180	90	90	90
2. Neutralizing additive	–	oil sh. ash	oil sh. ash	nepheline
3. Content of water-soluble form, %				
– Fe_2O_3, total	3.9	4.3	12.7	9.4
– of which FeO	0.9	1.2	3.2	2.8
– Al_2O_3	2.2	2.4	7.1	10.3
– K_2O	1.8	1.6	4.8	3.9
– MgO	0.9	1.1	3.2	1.2
– Na_2O	–	–	–	2.6
– CaO	–	0.08	0.24	0.26
– free H_2SO_4	5.4	0.7	–	–
4. Insoluble residue, %	–	–	2.8	11.7
5. Active element content in terms of Al_2O_3, %	4.7	5.2	15.2	16.3
6. Mass ratio $Al_2O_3 : Fe_2O_3$	0.56	0.56	0.56	1.09
7. Content of particles, %				
– +0.18–0.63 mm	–	–	54	72.5
– –0.05 mm	–	–	3	8
8. Requirement of materials for 1 g active elements, g				
– washed glauconitic sandstone	9.8	6	6.3	4.3
– sulphuric acid in terms of 100% H_2SO_4	6.6	4.9	5	4.3
– oil shale ash	–	1.8	1.9	–
– nepheline concentrate	–	–	–	1.3

for dissolving glauconite and in the kind of the neutralizing additive. Samples 1 and 2 are liquid, 3 and 4 solid coagulants. To obtain sample 1, the theoretically required amount of acid (100%) was used without neutralization of the reaction slurry. For producing sample 2, a 20% excess of acid was used and oil shale ash as neutralizing agent was added to the slurry. After that filtration followed. For producing sample 3, the liquid coagulant 2 was evaporated. In the process of obtaining sample 4, the excess acid amounted to 50%, the insoluble residue was separated by filtration, and the filtrate was neutralized with Kola nepheline concentrate. The mixture was subsequently processed into a solid product.

The samples of coagulants 1–4 and of solid wastes, washed and dried at 105 °C, were analysed in regard to the main chemical components, by ordinary methods. The content of microelements in the samples of mineral raw materials, coagulants, solid wastes, and the water, purified with coagulants 3–4, was determined by atomic absorption spectrometry (AAS, Pye Unicam 9100X, England). Photographs of samples of solid coagulants and wastes were made in the Centre for Materials Research of Tallinn Technical University by scanning electron microscope (SEM, Jeol JSM840A, Japan). Coagulant samples were examined also by X-ray powder diffraction techniques (DRON-4, CuK-radiation, Russia) and by differential thermal analysis (Q-1000, Hungary).

The efficiency of the coagulants was tested at the Laboratory of Tallinn Water Treatment Plant by conventional methods. The dose of the coagulants was constantly 16 mg/l in terms of Al_2O_3, as recommended on the basis of the earlier experiments [7]. The testing of the insoluble residue as an adsorbent for removing the PO_4^{3-} ion from the waste water was carried out by the method used in [8], with a few improvements.

RESULTS AND DISCUSSION

Characteristics of the coagulants

The chemical composition and the particle size analysis of the coagulant samples are reported in Table 1. The consumption of raw materials per 1 g of coagulant is presented as well.

Liquid coagulants 1 and 2 contain about 4% Fe_2O_3, over 2% Al_2O_3, the sum of AE being 4.7–5.2%. The mass ratio $Al_2O_3 : Fe_2O_3 = 0.56$ is somewhat higher than in the glauconite raw due to a better solubility of aluminium in sulphuric acid. Sample 1, obtained without using a neutralizing additive, contains 5.4% of free H_2SO_4. When oil shale ash was added the content of free acid decreased to 0.7% (sample 2).

Solid coagulants 3 and 4 contain three times more AE (15–16%) than the liquid ones. Sample 3 has the same ratio of $Al_2O_3 : Fe_2O_3$ as the liquid coagulant 2, because they are produced from identical materials. It contains about 13% Fe_2O_3 and 7% Al_2O_3. Besides water-soluble salts, the existence of 2.8% insoluble residue was detected. The latter probably represents yarosite-type ferric sulphates, e.g. $K[Fe_3(OH)_6(SO_4)_2]$, which precipitate as a result of hydrolysis at the stage of diluting the reaction slurry [5]. Coagulant 4 has a higher Al_2O_3 content (about 10%) because nepheline is added to neutralize the free acid. Therefore, $Al_2O_3 : Fe_2O_3$ mass ratio in this sample is twice as high as that in samples 1–3. On the other hand, product 4 differs from sample 3 in having a lower content of iron, potassium, and magnesium. The presence of a large amount of insoluble residue in sample 4 (nearly 12%) may be explained as resulting from a more intensive hydrolysis of iron due to the higher content of aluminium [2] and to the presence of undissolved nepheline. Samples 3

and 4 contain no free acid. More than half of the mass of these products consisted of particles coarser than 0.18 mm.

The requirement of the materials per 1 g of AE was the highest to obtain sample 1. For coagulants 2 and 3 the consumption of glauconite was about 1.5 times and the consumption of acid 1.3 times lower. The processing of the liquid coagulant 2 into a solid one (sample 3) caused a slight increase in the requirement of glauconite. Probably this phenomenon is connected with a decreasing content of water-soluble salts of iron in the course of evaporation. In the experiment for producing sample 4, with the addition of nepheline, the consumption of the acid and the summary requirement of mineral raws were somewhat lower than for sample 3. However, the use of imported nepheline may increase the price of the coagulant.

Our studies have shown that liquid coagulants represent an unstable system and during retention the precipitation of crystal salts was observed. Crystallization is induced by the hydrolysis and its intensity depends on the concentration of salts and free acid. For acidic solutions (sample 1) crystals appear after cooling down to the room temperature – about half an hour after the end of filtration. In the neutral liquid coagulant (sample 2) tiny crystals appear immediately after filtration.

The DTA curves together with the actual peak temperatures for sample 3 are shown in Fig. 1. Five endothermic peaks, caused by the loss of crystal water between 180 and 370 °C and the separation of SO_3 in the

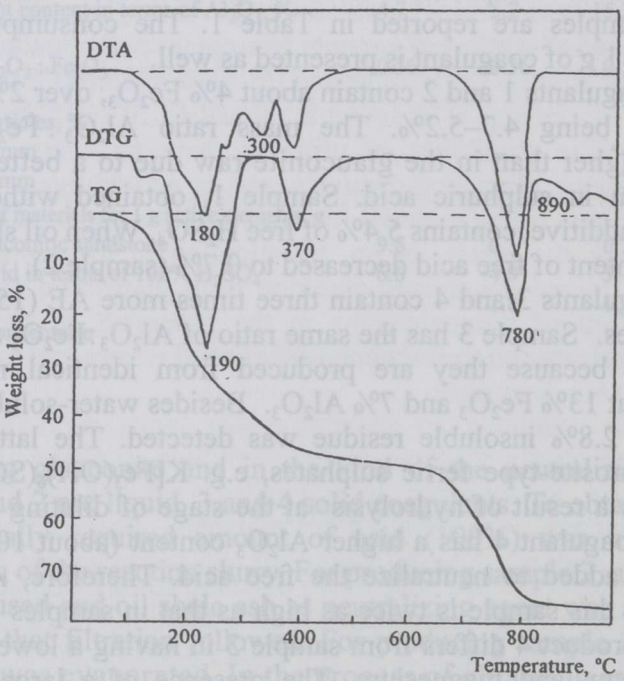


Fig. 1. Thermogram of coagulant sample 3 (see Table 1 for characteristics). Heating rate 10 deg/min, sample mass 616.7 mg.

range from 780 to 890 °C, were identified. Dehydration of $FeSO_4 \times 7H_2O$ begins already at 165 °C and ends at 320 °C. Thermal decomposition of iron(III) sulphate begins above 600 °C, of aluminium sulphate above 750 °C, of potassium and magnesium sulphates above 1000 °C, and of alum at 630 °C [2, 5]. The TG curve shows a mass loss up to 48.6% due to the vaporization of crystal water, and 25.9% due to the decomposition of sulphates and the separation of SO_3. The total content of SO_4^{2-} ion in the product according to chemical analysis is 57.4%.

An X-ray study of sample 3 (Fig. 2) showed the main components of this coagulant to be potassium alum and sulphates of aluminium, iron, and magnesium, containing various amounts of crystallization water [9]. Electron microscope photographs (Fig. 3) give evidence of the existence of such compounds as alunite $K_3Al_6(SO_4)_5(OH)_{10} \times 4H_2O$ and yarosite $K_2Fe_6(SO_4)_4(OH)_{12}$ in the coagulants in the form of quadratic and rectangular particles with variable degree of distinctness [5].

New coagulants in water purification process

The results of testing samples of refined Al–Fe coagulants obtained from glauconite are shown in Table 2. As reference materials three samples of industrial coagulants were used: aluminium sulphate from Sweden, iron(III) sulphate (42% solution, named PIX, product of *Kemivesi*, Tallinn), and unrefined coagulant produced from nepheline at *Eesti*

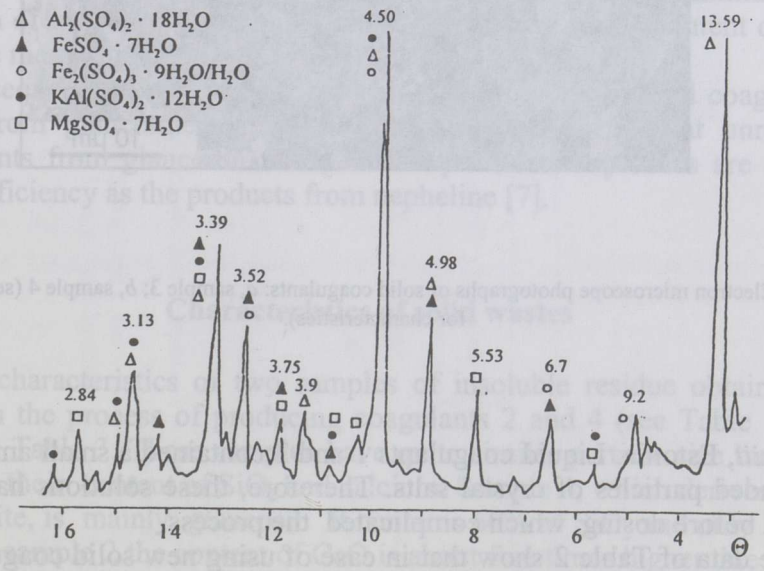
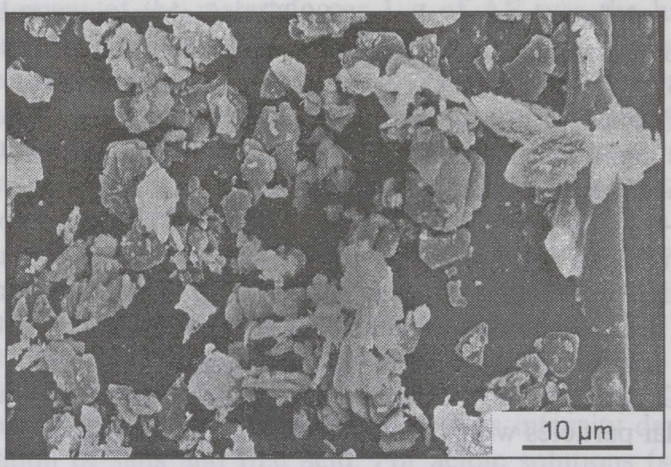


Fig. 2. X-ray diffractogram of coagulant sample 3 (see Table 1 for characteristics).

a



b

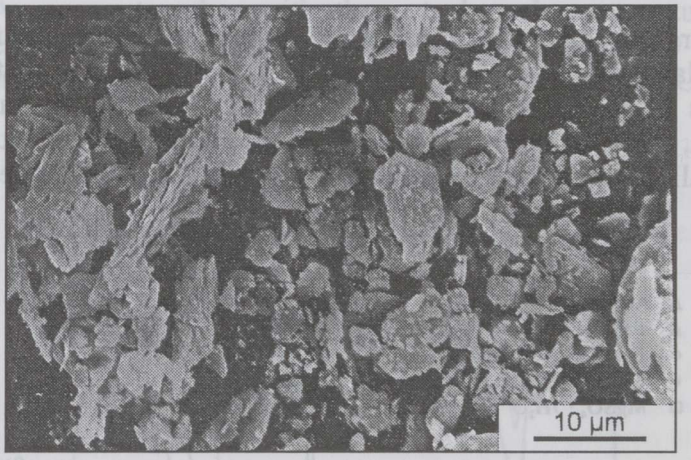


Fig. 3. Electron microscope photographs of solid coagulants: *a*, sample 3; *b*, sample 4 (see Table 1 for characteristics).

Fosforiit, Estonia. Liquid coagulants 1 and 2 contained a small amount of suspended particles of crystal salts. Therefore, these solutions had to be heated before dosing, which complicated the process.

The data of Table 2 show that in case of using new solid coagulants 3 and 4 the required quality of water, according to six controlled parameters, was gained. The other coagulants, including both laboratory samples of liquid ones and the industrial products, proved to be insufficiently effective

Coagulating ability of the products

Parameter	Permissible level	Raw water	Purified water after filtration						
			Coagulants from glauconite				$Al_2(SO_4)_3$	$Fe_2(SO_4)_3$	Unrefined coagulant from nepheline
			Liquid		Solid				
			1	2	3	4			
1. Turbidity, mg/l	1.5	16	1.2	1.8	1.1	0.8	1.2	1.7	1.4
2. Colour, °	20	27	5	6	11	7	6	9	6
3. pH	6.5–7.0	7.5	5.9	6.1	6.8	6.6	6.6	6.6	6.6
4. Content, mg/l									
Fe, total	0.3	0.07	2.03	1.21	0.12	0.05	0.08	0.41	0.11
Al^{3+}	0.2	0.06	0	0.01	0.02	0.03	0.64	0	0.57
5. Alkalinity, mg-eq./l	1.5–3.0	3.45	0.85	1.35	2.3	2.3	2.2	2.3	2.2

by one or two parameters under certain testing conditions. For example, in case of using liquid coagulants 1 and 2 the purified water contained too much iron and had an acidic reaction. The addition of aluminium sulphate or unrefined coagulant caused an increase in the content of aluminium, the addition of iron sulphate brought about an increase in the content of iron over the maximum permissible level.

Consequently, preference should be given to solid refined coagulants made from glauconite. It has been established earlier that unrefined coagulants from glauconite in the water purification process are of the same efficiency as the products from nepheline [7].

Characteristics of solid wastes

The characteristics of two samples of insoluble residue obtained as waste in the process of producing coagulants 2 and 4 (see Table 1) are given in Table 3. These samples have quite similar particle size but they differ in their content of SiO_2 and calcium. Sample 4, which derives from glauconite, is mainly glaucosil. It contains 66% of SiO_2 and only 3% of CaO. In sample 2 the content of CaO is about five times higher due to the use of oil shale ash, but the SiO_2 content is 10% lower. The presence of calcium sulphate crystals in sample 2 and different structural modifications of this salt may be observed in Fig. 4*a*.

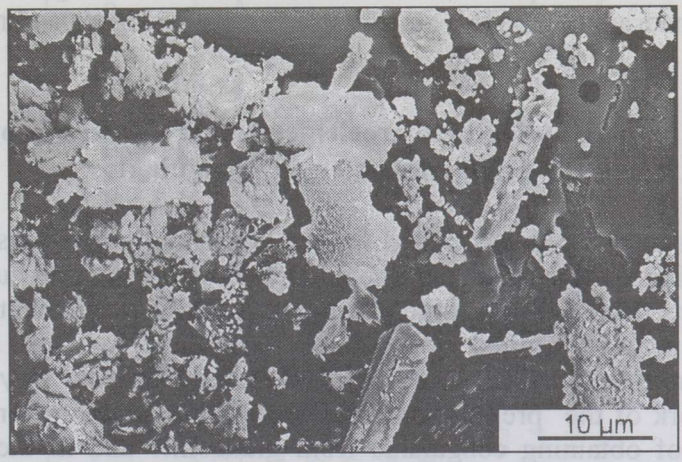
Table 3

Characterization of solid wastes

Sample*	Chemical composition, %								A	B	C
	Insoluble residue	SiO_2	Fe_2O_3	Al_2O_3	K_2O	MgO	CaO	SO_4^{2-}			
2	57.8	55.9	3.9	1	1.8	0.7	15	16.9	40	1.05/0.98	17
4	69	66.2	3.5	0.9	2.6	1.2	3	17.8	58	0.78/0.53	20

Notes: * See Table 1 for sample characteristics.
A – specific surface area, m^2/g;
B – amount of the waste, g per 1 g of glauconite/per 1 g of product;
C – adsorption ability of PO_4^{3-}, g per 1 g of solid waste.

a



b

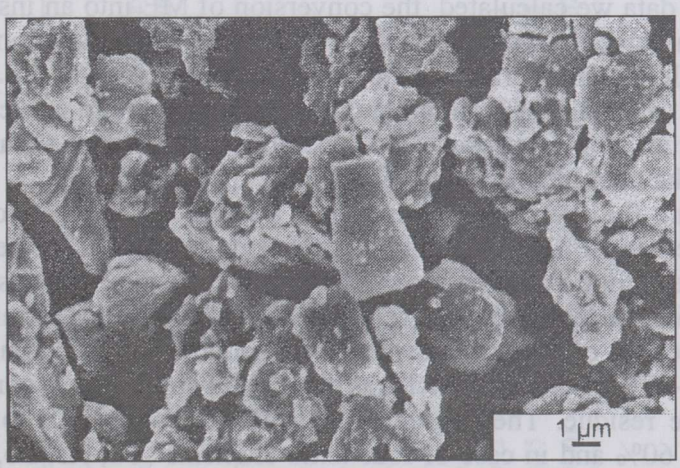


Fig. 4. Electron microscope photographs of solid wastes: *a*, sample 2; *b*, sample 4 (see Table1 for characteristics).

The testing of solid waste samples for removing PO_4^{3-} ions from water demonstrated the possibility of using these materials as adsorbents. The experiments showed that 1 g of solid waste adsorbed 17–20 mg PO_4^{3-}. This indicator was about the same for amorphous SiO_2 (aerosil) taken for comparison. Since the specific area of the waste samples (40 and 58 m^2/g) is much lower than that of aerosil (342 m^2/g), the relatively high efficiency of samples 2 and 4 may be explained by processes of chemosorption – formation of phosphates of calcium, aluminium, and iron.

The chemical composition of solid wastes suggests that they can be used also in other processes where materials containing calcium, silica, and sulphate are needed [6], for example, for producing expanding concretes.

Distribution of microelements in the processes of producing and using coagulants

Water used for drinking and for the household needs must have after purification an agreeable taste and odour and be harmless to human health. Therefore, the content of some heavy metals and toxic elements in purified water is severely limited by standards. Coagulants may also be regarded as potential sources of some toxic elements. That is why within the framework of the present work the distribution of microelements in the process of obtaining coagulants from glauconite and in the process of water purification was also studied.

Table 4 presents the content of microelements (ME) in the mineral raw materials, in the samples of solid waste, and in products 3 and 4. On basis of these data we calculated the conversion of ME into an insoluble form. In the calculations we took for coagulant 3 into consideration the input of ME with the main raw (glauconite) as well as with the neutralizing additive (oil shale ash). In other cases only glauconite was considered as the source of ME, because the insoluble residue was separated before adding the neutralizing agent (nepheline).

Among the raw materials oil shale ash has the highest content of the toxic elements Pb, Cd, As, and Hg. Glauconite contains more Cu and Zn, while nepheline contains more Mn and Cr. In the products made from glauconite the level of ME, excluding Cu, is lower than permitted for PIX [10]. The data of Table 4 show that in the process of producing coagulants only 45–47% of the Zn, which has the highest solubility, is converted to an insoluble residue. The degree of transition of other ME to solid waste exceeds 60% and in case of four toxic elements (Cu, As, Pb, Hg) it is as high as 75–100%.

Table 5 shows the content of ME in the water purified by using coagulants 3 and 4. The data presented show that the content of ME in the purified water is somewhat higher than in the raw water but it does not exceed the permissible level for drinking water [11]. Therefore, the solid coagulants made from glauconite may be used for water purification as far as public health service requirements are concerned.

CONCLUSIONS

The composition of refined Al–Fe coagulants obtained from glauconite and their efficiency in the water purification process are presented. Liquid coagulants contain 4.7–5.2% active elements in terms of Al_2O_3, solid ones

Table 4

Content of microelements in raw materials, products, and wastes*

Element	Content, mg per kg								Degree of transition into solid waste, %	
	Glauconite	Oil shale ash	Nepheline	Products		PIX, max. permissible level	Solid wastes			
				3	4		2	4	2	4
Cu	308	85	233	1.9	4.9	1	288	298	90.8	75
Zn	173	183	129	100	70	100	367	101	47	44.9
Mn	215	310	375	141	93	800	203	164	70.8	59.2
Cr	88	86	194	2.6	1.3	3	69	84	63.7	74.6
Ni	49	53	15	17	18	20	44	45	69.1	68.8
Pb	3.5	16	6	0.05	0.09	1	7.4	0.5	100	100
Cd	0.25	1.3	0.12	0.02	0.03	0.1	0.5	0.2	78.9	61.3
As	0.8	4.5	0.75	0.12	0.1	0.5	4.4	0.8	100	76.7
Hg	0.01	0.17	0.001	0.001	0.001	0.025	0.05	0.015	83.3	100

* The technological parameters see Table 1.

Table 5

Content of microelements in raw and purified water

Element	Content, mg/l			Max. permissible level, mg/l [11]
	Raw water	Purified water		
		Coagulant 3	Coagulant 4	
Cu	0.04	0.41	0.05	1
Zn	0.02	0.24	0.02	5
Mn	0.01	0.02	0.01	0.2
Cr	0.03	0.03	0.02	0.05
Ni	0.01	0.01	0.01	0.02
Pb	0.001	0.005	0.001	0.01
Cd	0.0001	0.0005	0.0001	0.003
As	0.003	0.002	0.003	0.01
Hg	0.001	0.001	0.001	0.001

15.2–16.3%. The type of the neutralizing additive has a significant influence on the composition and properties of coagulants. In case nepheline is used the $Al_2O_3 : Fe_2O_3$ mass ratio in the product increases up to 1.1.

The solid coagulant samples have good coagulating ability and they are stable. The use of liquid coagulants is more complicated because of their lower stability and lower efficiency in the water purification process.

The solid waste samples from the process of producing coagulants consist mainly of SiO_2 (glaucosil), with additives of calcium sulphate and insoluble residual material. The possibility of using these wastes for the adsorption of PO_4^{3-} ions from polluted water has been shown.

Our investigation showed that 60–100% of the total amount of the heavy metals and toxic elements in the mineral raw are converted into insoluble compounds in the process of obtaining coagulants and these are separated with the solid waste. The content of heavy metals and toxic elements in the water purified by the use of the coagulants obtained from glauconite did not exceed the permissible level.

ACKNOWLEDGEMENTS

The authors are grateful to the Estonian Science Foundation for financial support and to the Centre for Materials Research of Tallinn Technical University for SEM and X-ray measurements. The help of Mrs L. Põldoja in testing the coagulants and of Dr A.Viitak in AAS measurements is gratefully acknowledged.

REFERENCES

1. Kuusik, R., Viisimaa, L., Aasamäe, E. Refined coagulant for water purification from Estonian glauconite. I. Digesting glauconite with sulphuric acid in slurries. *Proc. Estonian Acad. Sci. Chem.*, 1996, **45**, 1/2, 42–55.
2. Zapolski, A. K., Baran, A. A. *Koagulyanty i flokulyanty v protsessakh ochistki vody.* Khimiya, Leningrad, 1987 (in Russian).
3. Johnson, P. N., Amirtharajah, A. Ferric chloride and alum as single and dual coagulants. *J. AWWA*, 1983, **75**, 5, 232–239.
4. Anso, J. *Glaukoniit kaalisoola allikana.* Teaduslik Kirjandus, Tartu, 1947.
5. Zapolski, A. K. *Sernokislotnaya pererabotka vysokokremnistogo alyuminiyevogo syr'ya.* Naukova dumka, Kiev, 1981 (in Russian).
6. *Tekhnologiya koagulyantov.* Khimiya, Leningrad, 1974 (in Russian).
7. Kudryavtseva, Ye., Viisimaa, L., Kuusik, R. A coagulant for water purification from Estonian glauconite. *Proc. Estonian Acad. Sci. Chem.*, 1994, **43**, 2, 68–76.
8. Roques, H., Nugroho-Jeudy, L., Lebugle, A. Phosphorus removal from wastewater by half-burned dolomite. *Wat. Res.*, 1991, **25**, 8, 959–965.
9. Mirkin, L. I. *Spravochnik po rentgeno-strukturnomu analizu polikristallov.* Izd. fiz.-mat. lit., Moskow, 1961 (in Russian).
10. *PIX koagulant.* Kemivesi, Tallinn, 1995.
11. *Joogivesi. Üldnõuded.* Eesti standard EVS 663:1995.

PUHASTATUD KOAGULANT EESTI GLAUKONIIDIST

II. Produktide ning jäätmete iseloomustus

Ludmilla VIISIMAA, Rein KUUSIK, Ernst AASAMÄE

On määratud puhastatud Al–Fe-koagulantide keemiline koostis ning omadused. Selgus, et vedelad produktid sisaldavad toimeaineid umbes 5%, tahked 15–16% (arvutatuna Al_2O_3-na). Uurides produktide kasutusvõimalusi veepuhastuses saadi mudeltingimustes parimad tulemused tahkete proovide puhul. Puhastatud vesi vastas nõuetele ka raskete ning toksiliste elementide osas. Tahke jääk sobib oma keemilise koostise poolest ehitusmaterjalide, sh. paisuvate betoonide tootmiseks, PO_4^{3-}-ioonide sidumisvõime tõttu ka adsorbendiks heitveepuhastuses.