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Effective laboratory-scaled ettringite precipitation of extractive waste influenced water with high sulphate content

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ABSTRACT

Extractive waste influenced waters or acidic mine drainages are of strong concern due to anionic pollutants such as sulphates as well as soluble forms of metals and metalloids, radionuclides, rare earth elements. Strict restrictions on the content of sulphates in waters along with other key parameters have been introduced in European legislation, consistent with the policies regarding the protection of water quality and human health. The present work examines the optimization of a proven in practice ettringite precipitation as a second step after liming in laboratory conditions in continuous mode with a pre-selected suitable source of aluminium in form of commercial cement. This allows reaching the ecological standards for sulphate content, as well as reducing the electrical conductivity in the effluent, thus eliminating the disadvantages of the classic scheme for lime treatment due to the high solubility of the formed precipitates of gypsum. However, the chemical composition and large quantities of formed sludge at the investigated method are still subject of particular attention from an economic and environmental point of view.

Keywords: sulphate removal, ettringite precipitation, extractive waste influenced waters.

INTRODUCTION

The sulphate anion is widespread in natural water ecosystems due to a variety of natural and anthropogenic sources - weathering of minerals, volcanic activity, transformations of organic matter, oxidation of sulphide minerals, formation of acidic mine drainages, pollution with agricultural and industrial wastewaters. The varying natural concentrations of sulphates in water bodies, depending on the local geophone related to the mineralization and hydrology of the region, must also be taken into account (Zak et al., 2021). The anthropogenically occurred sulphate discharges cause disturbance of natural biogeochemical cycles and acute ecological problems (Thomas et al., 2022). Reducing sulphate concentrations in water ecosystems is still an urgent challenge despite the relative low toxicity of the sulphate anion because of the wide range and extent of its release into nature. The discharge of industrial enriched with sulphates effluents leads to disturbance of the salt balance and salinization of fresh water thus endangering organisms that can only tolerate certain levels of water salinity. In addition, the prolonged consumption of drinking water with an increased sulphate content of over 0.5 g/L leads to gastrointestinal problems in humans (Chatla et al., 2023). Although there is a correlation between the sulphate content of natural surface waters and that of atmospheric sulphur dioxide, formed by fossil fuels combustion of and metallurgy, which on a global scale is decreasing, due to the large variety of other point and area sources of pollution, no decrease in the sulphate water load is observed.

Nowadays one of the main sources of sulphates in waters and soils is mining and extractive industry. The acidic extractive waste influenced waters (EWIW) or acidic mine drainages (AMD) are of a strong concern due to anionic pollutants such as sulphates as well as soluble forms of metals and metalloids, radionuclides, rare earth elements (Masindi et al., 2022). AMD are highly acidic aqueous solutions formed by chemical and/or biochemical oxidation in surface and shallow subsurface waters when rocks composed of sulphide-bearing minerals come into contact with water and oxygen thus forming sulphuric acid. Heavy metals are not biodegradable and tend to accumulate in living organisms, and many heavy metal ions are known to be toxic or carcinogenic. This type of waters should not be released into the environment without preliminary treatment (Oncel et al., 2013; Kruse Daniels et al., 2020).

Regarding the above-mentioned apprehensions, strict restrictions on the content of sulphates have been introduced in European legislations, consistent with the policies regarding the protection of water quality and human health. The precautionary threshold of sulphates in drinking water is 0.25 g/L as per Directive 2020/2184 on the quality of water intended for human consumption. The common individual emission limits (IELs) imposed on industrial mining operators are commonly in the range 0.25–0.50 g/L as a guideline for wastewater discharge.

The challenge of operators treating wastewater from mining and extractive industry is enormous (Matebese et al., 2024), due to various factors - extraction technology, sulphur content in the ore rocks, the available and applied treatment method. The average sulphates levels in EWIW after treatment are in the range 50–3000 mg/L (mainly metalliferous ores extractive waste management sites). In mine drainages formed as a result of the ore extraction in sulphide deposits, low pH values (below 5.00) are almost always found, alongside with excesses of IELs in relation to a number of indicators such as: electrical conductivity, sulphates, iron, copper, arsenic, zinc, etc. (Demir et al., 2020). The waters can also be characterized by high concentrations of aluminium and manganese. Due to ongoing processes of microbiological oxidation of ferro-ions, over time the pH in the waters decreases even more, and the course of this process is confirmed by the established increase in Eh values.

For the treatment of mine wastewater, rich in heavy metals and sulphates, different chemical methods are widely applied. Environmentally friendly at first sight passive treatment such as wetlands or alkalinity producing systems has low and insufficient removal efficiencies. Best Available Techniques Reference Document for the Management of Waste from Extractive Industries in accordance with Directive 2006/21/EC (MWEI BREF) states high removal efficiencies (~99%) when implementing some chemical treatment with mineral precipitation or membrane technologies. The classic cost-effective approach for treatment of wastewater with high sulphate concentrations is based on chemical precipitation using chemical reagents (Nurmesniemi et al. 2021). In these processes, precipitates are formed as a result of the formation of insoluble or low soluble chemical compounds - solid sulphate salts. The classical formation of gypsum through lime addition is not sufficient to reduce the sulphate concentration and EC values in EWIW below the IELs typical for mining sites operators (Nikolova et al., 2022), respectively 0.3 g/L and 1.8 mS/cm for industrial wastewaters before discharge. Lime ($Ca(OH)_2$) and limestone are typical neutralizing reagents for AMD as they reduce sulphate contents and metal ions in waters through precipitation of gypsum and formation of hydroxides. Although the gypsum is considered as moderate soluble, this depends the ionic strength of aqueous solution and the equilibrium concentration of SO_4^{2-} is in the range of 1.5–2 g/L (PA DEP-BAMR, 2019 and Cheong et al., 2022). The issue of treating the formed sludge also remains open, the management of which can be costly and environmentally challenging. More promising are the treatment methods with the formation of less soluble forms of sulphates with, such as ettringite and barium sulphate, with a twenty to thirty-fold greater reduction in sulphates compared to the lime treatment. When using barium salts for the barite precipitation, the treated wastewaters could meet the restriction levels for sulphates and heavy metals, but the method is controversial. The biggest disadvantage of using Ba is its toxicity, and in the case of $Ba(Cl)_2.2H_20$ – the concentration of free Cl-ions after the production of $BaSO_4$. Due to the presence of chlorine ions in the reagent the values of electrical conductivity exceed the IEL. It is extremely important the amount of barium to be equilibrium based, even a slight excess of the reagent could lead to the presence of barium ions in the treated waters. When treating real mine waters with varying quantities and concentrations of pollutants it is very difficult to be predicted and maintained the necessary ratio waters/reagent as well as the treated waters to be relevant to the legal norms. Another problem is that the process is reagent-intensive and results in the formation of significant amounts of precipitates – 3 kg of BaS per 1 m^3 of water with an initial sulphate concentration of 2 g/L results in 9 kg of sludge (Genova et al., 2023). Recommended method for lowering the sulphates contents and electrical conductivity is aluminium precipitation with the simultaneous formation of ettringite – $Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$ – hydrous calcium aluminium sulphate (Kabdaşlı et al., 2015). Ettringite precipitation has been developed as a reasonable alternative for sulphate-rich mine waters with sulphate concentrations over 2 g/L. This achieves a low concentration of 50–100 mg/l sulphate. The ettringite is stable above a pH of 10.7 and therefore the typical pretreatment is the addition of lime (Germishuizen et al., 2018).

The ettringite formation and precipitation requires blending of aluminium source and the pretreated mine water at an appropriate molar ratio of Al/SO_4. A prerequisite for effective removal of sulphates from wastewaters by ettringite precipitation was the maintenance of optimal pH, suitable ratio of $Ca/SO_4/Al$ – for example 3/6/2 (Niu et al., 2021, Zahedi et al., 2022) and sufficient residual time for stirring and precipitation. As stated in the studies (Zahedi and Mirmohammadi, 2022) three commercial processes use ettringite precipitation for sulphate concentration reduction with both metals precipitation and calcium sulphate (gypsum) formation as preliminary treatment steps. The Savannah Mining-Mintek process (SAVMIN) uses aluminium oxide (aluminium trihydroxide) to form the ettringite, with its recovery. The Cost-effective Sulphate Removal process (CESR) uses a proprietary Al containing chemical obtained from cement production, without recovery of the aluminium source and large amounts of formed sludges. The Outotec ettringite process or Walhalla Process uses sodium aluminate as a reagent which causes an excess of Sodium ions in treated waters.

As the typical aluminium sources as sodium or calcium aluminate or aluminium hydroxide are considered expensive (Tolonen et al., 2016) other reagents suitable for application in a larger scale are viral to be tested in order to be accepted as applicable in a real treatment facility for industrial impacted waters rich in sulphates. The present work examines the optimization of ettringite precipitation in laboratory conditions with a pre-selected suitable source of aluminium in continuous mode. In previous studies in batch mode (Nikolova et al., 2020) the aluminium cement proved to be the most suitable, as it allowed reaching the standards for sulphate content and electrical conductivity in the effluent.

MATERIALS AND METHODS

Feed solution and reagent

The operational water volumes with target pollutants were collected from an actual mining site with sulphide-rich ore body in the region of Srednogorie, Central Bulgaria. These effluents were defined as clarified Extractive Waste Influenced Water (EWIW) used as a feed solution for the laboratory-scaled treatment in continuous mode through ettringite formation. Regarding the EU law regulations, typical values in issuing permits for the discharge of wastewater into water bodies and determining individual emission limits for point sources of pollution, there could be pointed deviations of the norms for parameters pH, EC (µS/cm), sulphates, manganese, aluminium, copper and zinc in waters, taken from the mining site and used for the tests (Table 1). It should be noticed that IEL for sulphates in mining effluent is taken a value slightly higher to that for drinking water (0.3 g/L at 0.25 g/L for drinking water) but much lower than that causing gastroenteric problems (0.5–1.0 g/L) and for EC – even strict one (1800 µS/cm at a norm of 2500 µS/cm for drinking water).

As a cost-effective reagent available for industrial use was selected high aluminium cement with Al_2O_3 content in the range 50–60%, ($SiO_2 \leq 8\%$, $Fe_2O_3 \leq 2.5\%$, CaO – 30–39%) as the same showed good treatment qualities in the previous research, when it was test in batch mode in comparison with other sources of Al (Nikolova et al., 2020).

Design of the laboratory-scaled installation

The present laboratory study included a redesign of the operational mode of a laboratory-scaled installation (Fig. 1) from previous investigations for wastewater treatment by barite precipitation in continuous mode (Nikolova et al., 2022) in order to enhance sulphates and electrical conductivity reduction below the legislative norms. The model is based on the schematic implementation of CESR process as shown in studies (Liang et al, 2015).

Table 1. Average values of key indicators for the withdrawn water quantities

Indicator	Unit	Value	IELs
pH	–	**4.19±0.45**	6.00 – 9.00
EC	μS/cm	**3451±81**	1800
Eh	mV	381±52	–
SO_4^{2-}	mg/L	**1987±48**	300.00
Aluminium/Al		**6.53±0.06**	0.20
Arsenic/As		<0.01	0.10
Calcium/Ca		**857.91±48.41**	150.00*
Copper/Cu		**4.445±0.22**	0.10
Iron/Fe		1.01±0.12	3.50
Magnesium/Mg		30.72±0.47	80.00*
Manganese/Mn		**2.33±0.03**	0.05
Nickel/Ni		<0.01	0.20
Zinc/Zn		**3.60±0.09**	2.00

* Directive (EU) 2020/2184 on the quality of water intended for human consumption.

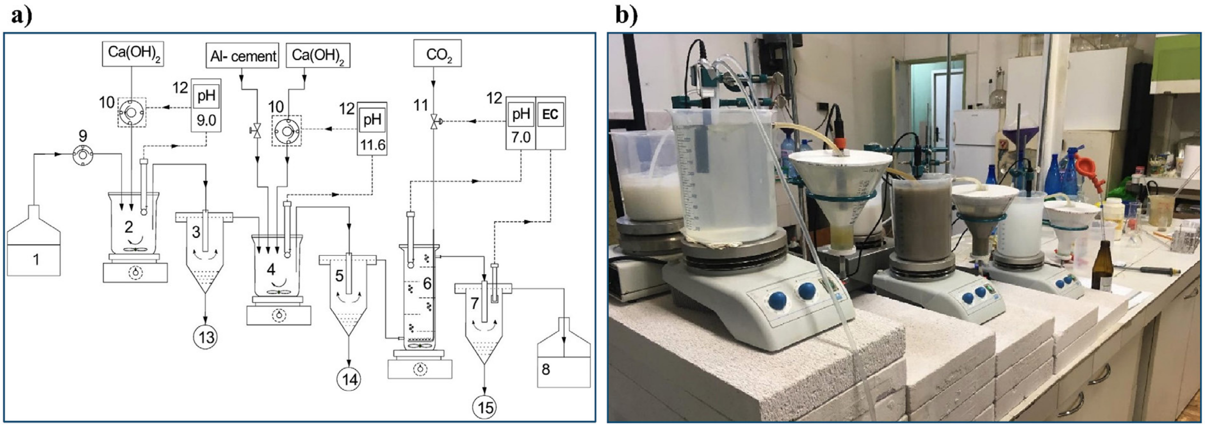

Figure 1. Flow-chart diagram (a) and layout (b) of the laboratory-scaled setup for ettringite precipitation in continuous mode: 1 – EWIW – feeding solution, 2 – reactor for initial neutralization, 3, 5, 7 – settlers, 4 – reactor for ettringite precipitation, 6 – column for decarbonization, 8 – collector tank, 9 – feed peristaltic pump, 10 – dosing pumps, 11 - gas electro-magnetic valve, 12 – pH controllers, 13 – sludge of hydroxides, 14 – ettringite sludge, 15 – carbonate sludge

The treatment process was performed at 22±°C in three steps: (1) preliminary addition of 3% (w/w) lime solution for the precipitation of heavy metals in form of hydroxides with partial reduction of sulphates concentration through gypsum formation; (2) ettringite precipitation with suitable reagents for the reduction of concentration of sulphates and electrical conductivity below IELs and (3) recarbonization for correction of pH and additional reduction of electrical conductivity. Each separate processes took place in a respective stirred reactor (2 L, 780 min^{-1}), cojoined with a respective radial flow settler (1.5 L). In each of one of the three chemical reactors the desired pH values were retained by precise peristaltic pumps dosing lime solution.

Analytical methods

The installation was set for online monitoring (sampling rate every 10 seconds) of pH in the reactors and of electrical conductivity in the settlers. The measuring of pH was performed by pH meter HANNA HI 9021 with VWR pH electrode. For the EC measurement was used WTW LF 197-S electrode. The sulphates were analyzed by spectrophotometric method with $BaCl_2.2H_2O$ at 420 nm wavelength of light. The Inductively Coupled Plasma (ICP) method was used for of heavy metals concentration determination. The sludges were observed with SEM JEOL JSM-6010PLUS/LA equipped with an energy dispersive spectrometer in order to perform elemental analysis.

RESULTS AND DISCUSSIONS

In order to investigate the influence of initial reagent dosage and pH on the efficient reduction below IELs of electric conductivity, sulphate content and target heavy metals contents at the ettringite precipitation different variants of case study simulations were performed (Table 2). The first set of experiments were conducted with different concentrations of A-cement (3.3, 5.0 and 6.0 g/L) in order to maintain an excess of Al for the suitable stochiometric ratio. The second set of experiments were at ascending pH values for the formation of ettringite. The different studied cases are given in Table 2 as the initial values of electrical conductivity and sulphates in the feeding solutions were respectively 3.45 µS/cm and 1.99 g/L.

It is confirmed that lime precipitation as a sole treatment method is insufficient to reduce the sulphate content and electrical conductivity below the normative limits (Table 3). Mendez-Ruiz et al. (2023) confirmed that lime treatment method is insufficient for a successful sulphate removal. However, this step is mandatory to precipitate heavy metals in the form of hydroxides. The subsequent ettringite precipitation process aims to reduce sulphate values and electrical conductivity below individual emission limits (Figures 2 and 3). Aiming at the normatively allowed pH values (6 to 9) for discharge after the ettringite precipitation process (usually optimal basic pH values) the posterior neutralization is performed via bubbling by carbon dioxide, as it is considered for an environmentally safe and inexpensive method (Tian et al., 2020).

The obtained results show that the use of aluminium cement in concentration of 3.33 g/L did not effectively reduce the concentration of sulphates and electrical conductivity. Significantly better results in a comparison with these were obtained when using aluminium cement in a concentration of 5 or 6 g/L maintaining pH of 11.5 in the reactor for the formation of ettringite. The sulphates concentration and electrical conductivity at the outlet of the laboratory installation were at the limit of IELs for variant 2-A and slightly below for variant 3. In the third experiment (variant 3) with aluminium cement of 6 g/L, in addition to the increase of the concentration of cement, the flow rate of the treated water was also increased by 20%. The use of aluminium cement at a concentration of 6 g/L and the maintenance a pH of 11.5 for ettringite precipitation effectively achieved the removal of sulphates from the water and reduced the electrical conductivity.

Table 2. Different variants of case study simulations for ettringite precipitation of EWIW

Variant	Al cement, g/L	Flow-rate, L/h	pH for EP	$Ca/SO_4/Al$	Residual time, h		pH for recarb.
					In reactors	In settlers	
1	3.33	1.00	11.5	1.12/1.99/0.44	2.00	1.00	7.00
2-A	5.00	1.00	11.5	1.19/1.99/0.66	2.00	1.00	7.00
2-B		1.20	11.7	1.21/1.99/0.66	1.67	0.83	7.00
2-C		1.20	11.9	1.22/1.99/0.66	1.67	0.83	7.00
2-D		1.20	12.1	1.23/1.99/0.66	1.67	0.83	7.00
3	6.00	1.20	11.5	1.61/1.99/0.80	1.67	0.83	7.00

Table 3. Sulphates and electrical conductivity variations in different variants during lime pre-treatment

h	Sulphates, g/L							EC, µg/cm						
	1	2-A	2-B	2-C	2-D	3	IEL	1	2-A	2-B	2-C	2-D	3	IEL
1	1.99	1.98	1.97	1.96	1.96	1.99	0.3	3444	3451	3472	3441	3446	3458	1800
2	1.96	1.97	1.96	1.94	1.96	1.97		3434	3442	3459	3445	3442	3451	
3	1.97	1.93	1.97	1.92	1.95	1.98		3449	3441	3461	3439	3448	3445	
4	1.99	1.95	1.93	1.9	1.92	1.96		3469	3444	3457	3445	3443	3462	
5	1.92	1.97	1.95	1.96	1.94	1.95		3424	3445	3435	3443	3444	3446	
6	1.96	1.94	1.98	1.99	1.95	1.97		3442	3432	3427	3451	3442	3442	
7	1.94	1.98	1.98	1.97	1.97	1.97		3404	3430	3440	3445	3451	3459	
8	1.99	1.96	1.99	1.97	1.98	1.99		3442	3428	3445	3441	3447	3452	

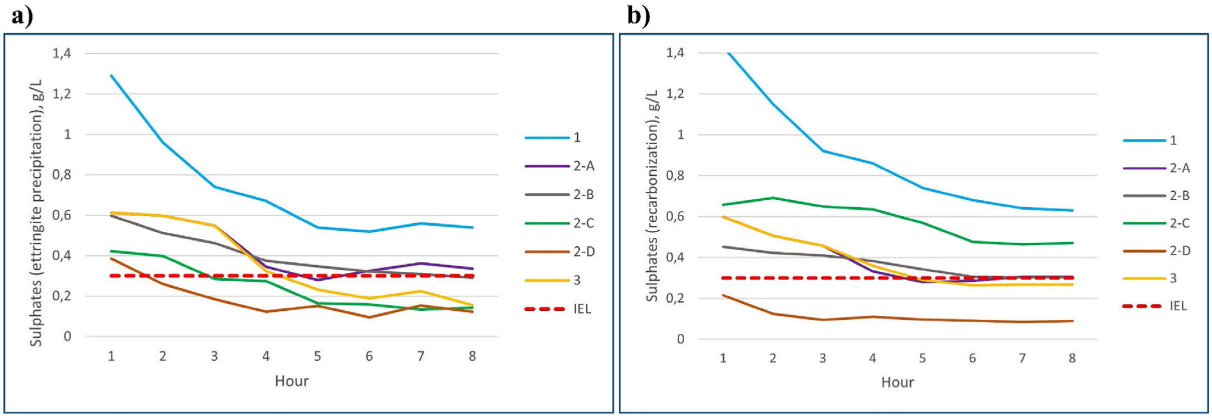

Figure 2. Sulphates reduction in (a) ettringite precipitation and (b) recarbonization phases

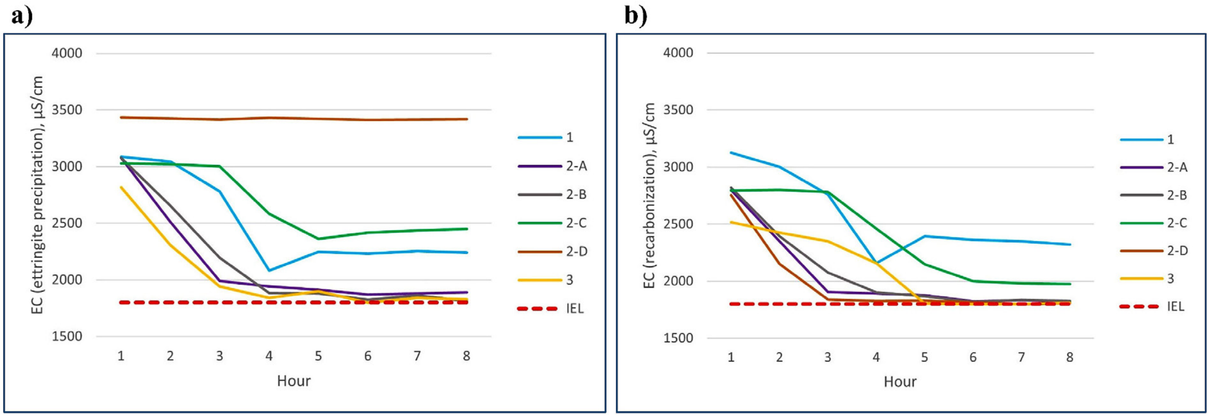

Figure 3. Electrical conductivity in (a) ettringite precipitation and (b) recarbonization phases

The first series of experiments on the optimization of ettringite precipitation for the treatment of mine waters at pH 11.5 with the use of aluminium cement as a reagent showed that at the use of Al-cement in a concentration of 5 g/l, IELs for sulphates and conductivity values are exactly reached, which is a prerequisite for their exceeding in the event of variations in any of the various operational parameters of the process – the flow rate and chemical composition of the treated water, the qualitative composition of the cement, the maintained pH in the separate reactors for lime treatment, ettringite precipitation and recarbonization, failures with reagent dosing and equipment, etc. For this reason, a second series of experiments was conducted to investigate the influence of pH on the formation of ettringite and on reduction of sulphates and electrical conductivity below acceptable values with a reasonable margin. The variant with 5 g/L of cement was chosen as the most economically advantageous, i.e. the minimum amount of aluminium source for ettringite precipitation at which an efficient treatment process is achieved – case studies 2-B, 2-C and 2-D. Regarding the relation between pH and removal of sulphates from wastewater by the ettringite precipitation using aluminium cement reagent 5 g/L it could be concluded that an effective removal of sulphates with an initial concentration at about 2 g/L was achieved maintaining the pH in the range 11.9–12.1. Zahedi et al. (2022) reported just a little higher optimal pH range of 12 to12.5. Some other authors had noted the minimal effect of pH variation on the efficiency of the process if it ranges at high pH values (Benatti et al., 2009; Almasri et al., 2015).

In summary, variants 2-B and 3 successfully reached the two limits of 0.3 mg/L and 1800 µS/cm for sulphates and electrical conductivity, respectively. In addition, options 2-A and 2-D are suitable in terms of reducing electrical conductivity, and option 2-A (5 g/L aluminium cement) still slightly exceeded the IEL at the eighth hour. Regarding the heavy metals` precipitation, the smaller content of Al-source was not enough for reducing the concentrations of Cu and

Al in the effluents below the IELs (Table 4). The other variants cover the most restrictive EU legal obligations concerning the target heavy metals even for drinking and domestic purposes.

The sulphate removal efficiencies after finalizing the recarbonization are in the range of 68.3 to 95.5 % (1 – 68.3%, 2-A – 85%, 2-B – 84.7%, 2-C – 76.3%, 2-D – 95.5%, 3 – 86.6%) as the required rate is 84.9%. The studied process under different operational conditions could be efficiently implement only with EWIW relatively poor in Mg, as in its presence preferentially will be formed precipitates of $Mg_4Al_2(OH)_{14}.3H_2O$ or $MgAl(OH)_{14}.XH_2O$ (Niu et al., 2021). In the tested solutions Mg concentrations are still present. Dou et al. (2017) stated that in absence of Mg^{2+}, the optimum sulfate removal of 99.7% was obtained. That could be related to the highest obtained rate of sulphate removal at variant 2-D, taking into account the inhibition effect of the initial concentration of Mg and the different tested calcium/sulphate/aluminium ratios.

The use of aluminium cement at a concentration of 6 g/L and the maintanance a pH of 11.5 for ettringite precipitation effectively achieved the removal of sulphates from the water and reduced the electrical conductivity firstly and in addition the heavy metals at the outlet were below the IELs except for the Al. The water contained relatively high concentrations of aluminium (0.21–4.11 mg/L – Table 3) due to fluctuations in pH in the recarbonization reactor for all tested variants. In variant 2-C after the recarbonization, the concentration of sulphates increased, which was due to the transport of fine particles of ettringite, which dissolved with the decrease of the alkaline reaction. In this experiment, the pH in reactor 3 was maintained in the range of 6.8–7.5. At these values, however, the necessary removal of dissolved aluminium was not achieved. From the obtained results it could be concluded that the pH in the recarbonization reactor must be maintained below 7.

The aluminium cement before use and ettringite sludge formed at pH 12.1 were analyzed by SEM (Figs. 4 and 5). The precipitates included mainly O (clearly visible peak, over 45%) and Ca (21%). Relatively low concentrations of heavy metals are observed, due their removal in

Table 4. Heavy metals concentrations in the outlet solution at the 12th hour

Variant	Al	Ca	Cu	Fe	Zn
	mg/L				
1	**0.21**	187.8	**0.119**	<0.03	**0.020**
2-A	**0.31**	**746.6**	<0.005	<0.03	0.008
2-B	**2.59**	**258.9**	<0.005	<0.03	<0.005
2-C	**4.11**	43.2	<0.005	<0.03	<0.005
2-D	**1.81**	103.9	<0.005	<0.03	<0.005
3	**1.55**	<0.03	<0.005	<0.03	<0.005
IELs	*0.2*	*150*	*0.1*	*3.5*	*2.0*

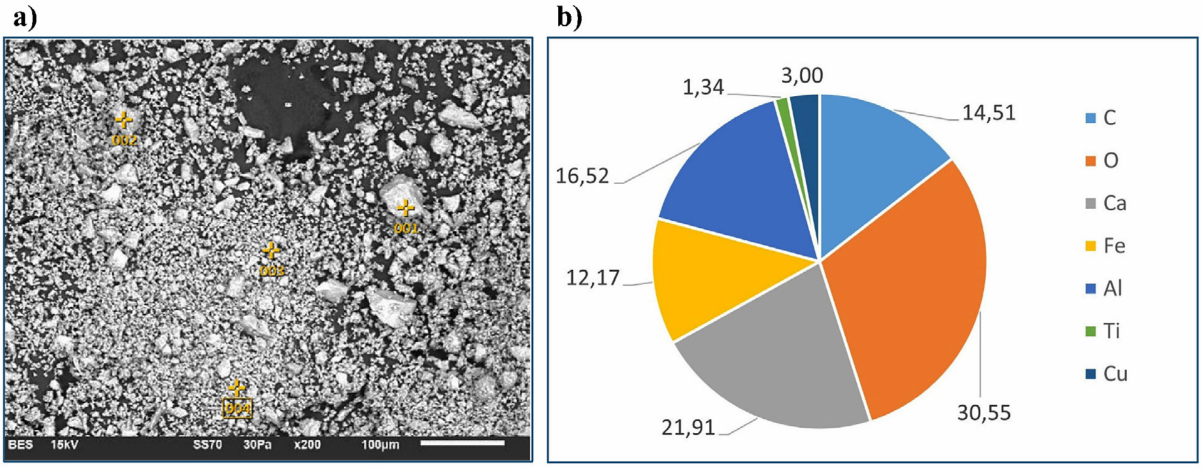

Figure 4. SEM image (a) and elemental composition (b) of Al-cement before treatment – the elemental composition is in percentages

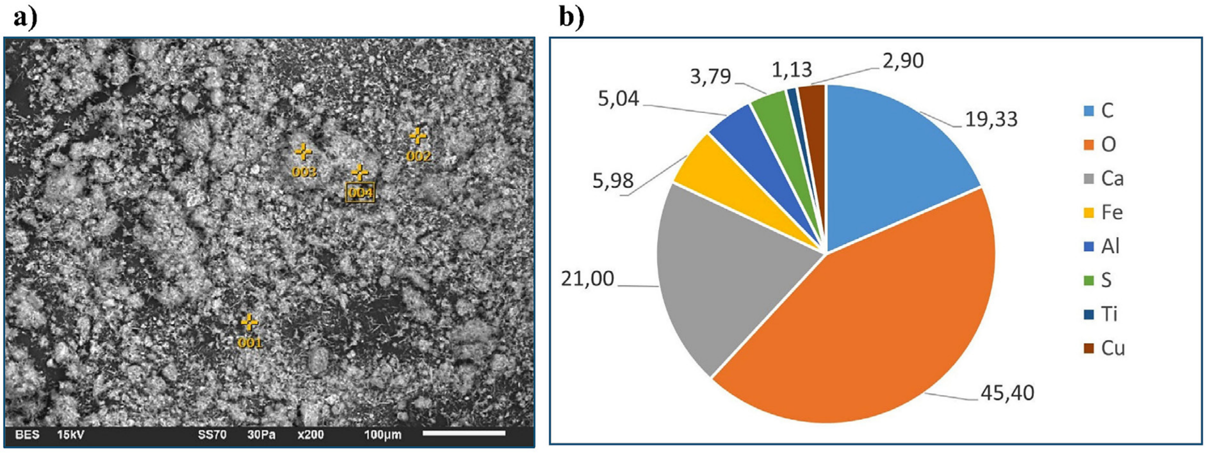

Figure 5. SEM image (a) and elemental composition (b) of sludge after ettringite treatment with Al-cement 5.0 g/L at pH 12.1 (a), the elemental composition is in percentages (b)

the previous step of lime treatment (Nikolova et al., 2020) – Fe (over 39%), Cu (8%) Zn (3.5%), as the Al is in the same range (4–5%). Moreover, an average sample of the formed sludges after ettringite precipitation with Al-cement at pH 12.1 was given for silicate analysis and the data from it are as follow (in %): Al_2O_3 – 13.05, CaO – 31.98, Fe_2O_3 – 5.27, K_2O – 0.20, MgO – 0.57, MnO – 0.01, Na_2O – 0.39, P_2O_5 < 0.05, SiO_2 – 6.87, SO_3 – 15.43, TiO_2 – 0.64, loss on ignition – 26.46. The content of heavy metals and metalloids is as follows (in mg/kg): As – <10, Cd <1, Co – 10.5, Cr – 140, Cu – 91.3, Hg < 1, Mn - 178, Ni – 58.5, Pb <10, Sb <10 and V – 105. Considering the above-mentioned elemental composition and according to the European Waste Catalogue (EWC) the sludge is classified with Code 06 05 02* – sludges from on-site effluent treatment containing hazardous substances (Mirror Hazardous code). The formed sludges of aluminium cement and ettringite were characterized by large volumes. The sludges were significantly more hydrated than that obtained in the batch experiments in periodic mode (Nikolova et al., 2020). This led to the need to ensure the necessary residual time in the settler for ettringite precipitation, constant removal of the formed sludge and its dehydration during the realization of the EWIW treatment through the use of aluminium cement as a reagent. For these reasons, it is of a great importance to foresee the management of the formed ettringite sludges. There was made an indicative balance (Table 5) of the quantities of the formed sludges and used reagents. The question of the operational costs when using this treatment method remains open. From an economic point of view, the possibility of utilizing sludge in the production of cement and concrete is important. Tian et al. (2019) reported that Al-recovery could lower the operational and maintenance cost of the process by about and over 1/3. They proposed a novel sulphate removal process with ettringite precipitation under low pH condition. Another innovative and promising approach for performing ettringite precipitation is an electrochemical Al-dosage but needs further improvements as the cost was still slightly higher than the cost of classical aluminium salts (Nurmesniemi et al., 2021).

Table 5. Balance of quantities of reagents and formed precipitates in the treatment of clarified EWIW

Process	Reagent	Treatment of 100 000 m³	
		Reagent, t	Sludge, t
Liming pH 9.0	$Ca(OH)_2$	25–30	45–50
Ettringite precipitation Al-cement 5.0 g/L pH 11.5	$Ca(OH)_2$	120	910–970
	Al-cement	600	
Ettringite precipitation Al-cement 5.0 g/L pH 12.1	$Ca(OH)_2$	250	890–940
	Al-cement	500	

CONCLUSIONS

Based on the obtained results some conclusions could be made.

1. The first phase of treatment is liming. Heavy metals are effectively removed, but due to the high solubility of gypsum, IELs for electrical conductivity and sulphates cannot be achieved.
2. Sulphur compounds were not found in the Al-cement. After ettringite precipitation, there was observed sulphur in the sludge from 3.8 to 8.5%.
3. At the ettringite precipitation the aluminium dissolved, as the concentration of Al in the waters increased with the higher pH values.
4. The dissolved aluminium precipitates as a hydroxide in the recarbonization process.
5. The precipitates formed at the process of ettringite precipitation are in large quantities.
6. In order to make a final decision on the choice of technology applicable for the specific wastewater treatment before discharge it is of an emerge importance to focus on the possibility of utilization of sludge in the production of cement and concrete or as a sorbent.

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