

## POSSIBILITY OF USING A MIXTURE OF CALCIUM SALTS TO DECREASE SULPHATE CONCENTRATION AND TOTAL MINERALISATION OF SURFACE AND MINE WATERS

Yuliia Trach<sup>1</sup>, Roman Trach<sup>2</sup>✉

<sup>1</sup>Department of Water Supply, Water Disposal and Drilling Engineering, National University of Water and Environmental Engineering, Rivne, Ukraine

<sup>2</sup>Institute of Civil Engineering, Warsaw University of Life Sciences – SGGW, Warsaw, Poland

### ABSTRACT

Natural limestone may be an option for removing sulphates from water. Such waters, which contain high concentrations of sulphate ions, are surface and mine waters. In this work, the removal of sulphate from model solutions (pH 6–8) by their sorption and chemical binding with calcium salts was studied. For experimental studies, natural limestone was taken, which was crushed to 1–10 µm. Such limestone was modified with acetic acid. A mixture of grinding limestone with the obtained calcium acetate was used for research. Experiments conducted in static conditions showed a decrease in sulphate concentration from 1.2 to 0.38 mg·dm<sup>-3</sup> for a duration of 3 days and adding CaCO<sub>3</sub>:Ca(CH<sub>3</sub>COO)<sub>2</sub> in a ratio of 1 : 1. The analysis of various scientific studies allowed us to assume that when such a mixture of calcium salts is used to reduce sulphate ions in natural surface waters, the formed acetate ion will undergo biological degradation. Thus, it is possible to achieve a reduction in the total mineralisation of surface waters.

**Key words:** sulphates, surface water, limestone, acetate calcium

### INTRODUCTION

Sulphate ions (SO<sub>4</sub><sup>2-</sup>) are the main anions that are found in high concentrations both in natural waters and in industrial wastewater, as well as in the drainage of mines. Compared to toxic anions (such as nitrates, chromates, or manganates), sulphates are moderately dangerous (Schultze, Bohrer, Kuehn & Büttner, 2002). Therefore, in many countries of the world, there are no established recommendations for sulphates in drinking water. These anions affect the taste of water and, in high concentrations, can negatively affect the human digestive system (Trach, 2020; Trach, Tytkowska-Owerko, Reczek & Michel, 2021). Therefore, environmental protection authorities in many countries have established a permissible range

of sulphate ion concentration values, namely from 250 to 500 mg·dm<sup>-3</sup> (United States Environmental Protection Agency [US EPA], 1986).

The most important source of higher concentrations of sulphates is the leakage of mine waters into natural surface waters. The process of industrial extraction of metals from sulphide ores is always accompanied by the formation of a very large amount of mine water. Such mine waters, in addition to a high concentration of sulphates, have a high total mineralisation. Due to the fact that mine waters are very often produced in large volumes, there is a problem with their purification from sulphates and limiting the mineralisation of these waters. Very often, mine water is sent through canals from the mine to natural water reservoirs. Such objects can be rivers or artificial lakes that collect

mine water before releasing it into rivers, so as a result of mining processes, surface water is polluted, so there is a need to find a way to treat it.

Treatment of a large volume of natural water from sulphates is a difficult task (Roonasi & Holmgren, 2009; Choudhary & Sheoran, 2012; Runtti et al., 2017). Today, there are the following sulphate removal methods, namely:

- sorption technologies, including the use of membranes and ion exchange resins;
- chemical precipitation in the form of barium sulphate, gypsum or ettringite  $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}]$ ;
- biological with the help of sulphate-reducing bacteria.

Calcium compounds are used to reduce the concentration of sulphates in surface waters. Such compounds are quicklime and natural limestone. It is known that the dissociation of natural limestone in water occurs slowly; as a result, the concentration of calcium ions ( $\text{Ca}^{2+}$ ) is insufficient to bind  $\text{SO}_4^{2-}$ . This is the main problem of purifying natural waters from sulphates. In addition, methods of reducing the concentration of sulphates in water with the addition of pure limestone are ineffective if the pH of the water is 6–8 or the concentration of  $\text{SO}_4^{2-}$  in the reservoir is not very high (Davis, Webb, Sorensen, Dixon & Hudson, 2018).

Yanamadala (2005) reported on the use of limestone activated by acids, e.g. hydrochloric acid. This method allows for reducing the concentration of  $\text{SO}_4^{2-}$  in water, however, after adding such limestone, an excess of environmentally unfavourable chloride ions ( $\text{Cl}^-$ ) appears in the water, and the overall mineralisation of the water remains practically unchanged. When water is saturated with  $\text{Ca}^{2+}$  in an amount of at least  $0.2 \text{ g}\cdot\text{dm}^{-3}$ , the formation of insoluble calcium sulphate ( $\text{CaSO}_4$ ) is possible (Kim & Park, 2008). The solubility of calcium carbonate ( $\text{CaCO}_3$ ) is low and decreases with increasing mineralisation, creating problems related to the formation of ionised calcium in the water.

The purpose of the research was to compare the effectiveness of reducing the concentration of sulphate ions and the general mineralisation of water by adding mixtures of insoluble and soluble calcium salts (calcium carbonate and acetate) in different doses, and also assessment of the possibility of biological decomposition of acetate ions ( $\text{CH}_3\text{COO}^-$ ).

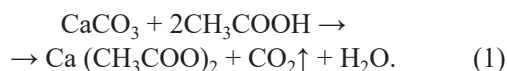
## MATERIAL AND METHODS

Mineral phase analysis of natural limestone was carried out using an Aeris Minerals PANanalytical diffractometer (Malvern Panalytical, Malvern, UK).

The test material is a mixture of calcium carbonate and calcium acetate, characterised in that the weight ratio of the mixture of calcium carbonate and calcium acetate is from 1 : 1 to 4 : 1, respectively. The mixture is characterised by the fact that the grain size of calcium carbonate and calcium acetate does not exceed  $10 \mu\text{m}$ .

The peculiarity of the calcium carbonate and calcium acetate, is characterised by the fact that the limestone was subjected to grinding, and then, with continuous stirring, an aqueous solution of acetic acid was added to the limestone in an amount enabling the final weight ratio of the  $\text{CaCO}_3:\text{Ca}(\text{CH}_3\text{COO})_2$  mixture to be from 1 : 1 to 4 : 1, after which the resulting mixture is subjected to drying.

The method of preparing the test mixture consisted in adding dry, ground limestone to the water, previously chemically activated with acetic acid, in order to treat natural surface and mine waters. During the chemical treatment of dispersed limestone with acetic acid, the following chemical reaction occurs:



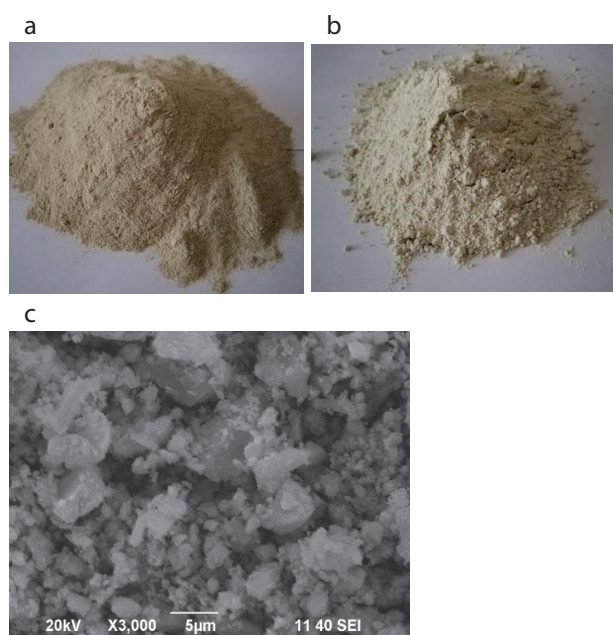
A Mastersizer 2000 laser sedimentograph with a Hydro 2000S liquid dispersion module (Malvern Instruments, UK) was used to analyse the particle size composition of the samples. Mastersizer 2000 is a modern high-tech particle size analyser, the principle of which is based on laser diffraction of light. The measurement range is  $0.02\text{--}2,000 \mu\text{m}$ . Particles in a parallel laser beam scatter light at a constant angle, the value of which depends on their diameter, and for granulometric analysis, it is necessary to set such optical characteristics as the degree of absorption and refractive indices. The Hydro 2000S liquid dispersion module is used to study samples with pellet-sized particles. A suspension based on distilled water is prepared for the analysis.

Natural limestone with a particle size of not more than  $50 \text{ mm}$  was ground until particles with a grain size of not more than  $1 \mu\text{m}$  were obtained. The limestone

is then placed in a vessel with a mechanical stirrer, and a concentrated solution of acetic acid with a minimum concentration of 30% is added, in an amount enabling the final weight ratio of the mixture containing  $\text{CaCO}_3:\text{Ca}(\text{CH}_3\text{COO})_2$  to be 1 : 1. Depending on the concentration of sulphate ions in the water reservoir to which the mixture of calcium carbonate and calcium acetate is added, the final weight ratio of the mixture containing  $\text{CaCO}_3:\text{Ca}(\text{CH}_3\text{COO})_2$  may be 1 : 1–4 : 1, respectively. After the addition of the aqueous acetic acid solution is complete, stirring is continued for at least 2 h, and then the resulting mixture of  $\text{CaCO}_3:\text{Ca}(\text{CH}_3\text{COO})_2$  is dried at room temperature until completely dry.

## RESULTS AND DISCUSSION

The experimental studies carried out showed the following results – the general appearance of the studied limestone before and after grinding, as well as under an electron microscope, can be seen in Figure 1.

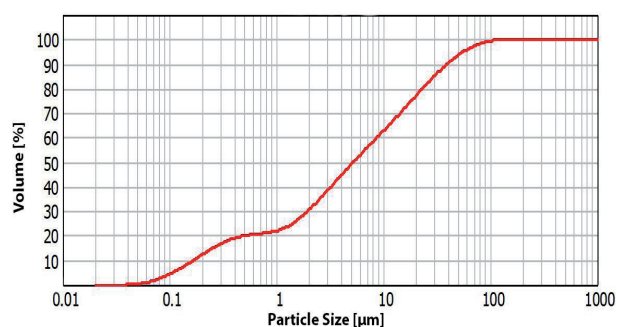


**Fig. 1.** Appearance of the studied limestone before and after grinding, and under an electron microscope: a – limestone before grinding; b – limestone after grinding; c – limestone after grinding

Source: own work.

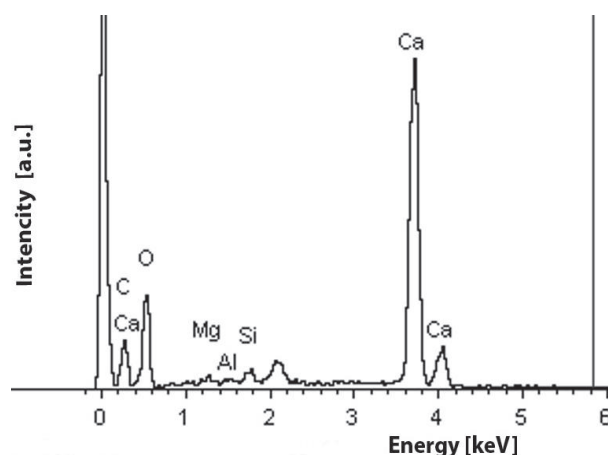
The results of determining the grain composition of crushed natural limestone can be seen on the differential curve of particle size distribution in Figure 2.

X-ray analysis of the natural limestone under study showed that the dominant mineral is limestone (more than 96%). The obtained diffractogram is presented in Figure 3.



**Fig. 2.** Differential curve of particle size distribution

Source: own work.



**Fig. 3.** X-ray diffractogram of the studied natural limestone

Source: own work.

The mixture for reducing the concentration of sulphates and general mineralisation of surface and mine waters contains calcium carbonate and calcium acetate, the grain size of which is not more than 10 µm, and the final weight ratio of the  $\text{CaCO}_3:\text{Ca}(\text{CH}_3\text{COO})_2$  mixture is 1 : 1–4 : 1, respectively (Table 1).

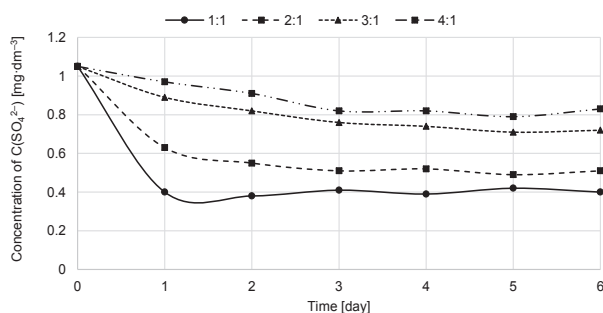
**Table 1.** Composition of a mixture of  $\text{CaCO}_3$  and  $\text{Ca}(\text{CH}_3\text{COO})_2$  with different weight ratios

Parameter	Mass ratio of $\text{CaCO}_3$ : $\text{Ca}(\text{CH}_3\text{COO})_2$			
	1 : 1	2 : 1	3 : 1	4 : 1
Weight of calcium carbonate ( $\text{CaCO}_3$ ) [kg]	1.63	2.63	3.63	4.63
Weight of 30% acetic acid solution ( $\text{CH}_3\text{COOH}$ ) [kg]	2.53	2.53	2.53	2.53

Source: own work.

Experimental studies were carried out with model solutions at 15°C. The initial pH values of the water samples were 6, 7 and 8, and the total mineralisation of dissolved substances in the water (total dissolved solids – *TDS*) was assumed to be 0.02, 0.5 and 1.5 g·dm<sup>-3</sup>. The pH of the water samples was adjusted using 0.1M HCl and 0.1M NaOH solutions, and the *TDS* of the water was adjusted using a 0.1M NaCl solution. Such parameters of model samples were adopted in order to carry out experimental research as close as possible to natural conditions. The concentration of sulphate ions in the model solutions was 1.05 g·dm<sup>-3</sup>. Plastic vials with a capacity of 200 ml were used for experimental studies. The volume of the tested solution was assumed as 150 ml. Chemically activated

calcium carbonate was added to the model solutions in the following proportions of  $\text{CaCO}_3$ : $\text{Ca}(\text{CH}_3\text{COO})_2$  – 1 : 1, 2 : 1, 3 : 1 and 4 : 1. The dose of chemically activated limestone in the indicated proportions was 2 g·dm<sup>-3</sup>, respectively (Table 2). Experimental studies were carried out for 6 days, with the daily determination of the concentration of sulphate ions in the solutions. The results of the experimental studies are presented in Figure 4.



**Fig. 4.** Dependence of the removal of sulphate ions in time on the proportional content of  $\text{CaCO}_3$  and  $\text{Ca}(\text{CH}_3\text{COO})_2$

Source: own work.

Treatment of the dispersed limestone with acetic acid, followed by its drying, makes it possible to obtain a mixture of  $\text{CaCO}_3$  and  $\text{Ca}(\text{CH}_3\text{COO})_2$ . After

**Table 2.** Concentration of sulphates after adding the calcium mixture during chemical equilibrium (initial sulphate concentration 1.05 g·dm<sup>-3</sup>, dose of the mixture 2 g·dm<sup>-3</sup>)

Model solution $\text{CaCO}_3$ : $\text{Ca}(\text{CH}_3\text{COO})_2$	pH	Total dissolved solids ( <i>TDS</i> ) [g·dm <sup>-3</sup> ]	Concentration of $\text{C}(\text{SO}_4^{2-})$ [g·dm <sup>-3</sup> ]		pH	Total dissolved solids ( <i>TDS</i> ) [g·dm <sup>-3</sup> ]	Concentration of $\text{C}(\text{SO}_4^{2-})$ [d·cm <sup>-3</sup> ]	
			Initial	Final			Initial	Final
1 : 1	6		1.05	0.22	6		0.29	0.42
	7	0.02	1.05	0.31	7	0.5	0.42	0.56
	8		1.05	0.62	8		0.64	0.73
2 : 1	6		1.05	0.29	6		0.44	0.51
	7	0.02	1.05	0.42	7	0.5	0.51	0.67
	8		1.05	0.69	8		0.74	0.86
3 : 1	6		1.05	0.38	6		0.63	0.75
	7	0.02	1.05	0.61	7	0.5	0.72	0.89
	8		1.05	0.78	8		0.83	0.91
4 : 1	6		1.05	0.61	6		0.72	0.87
	7	0.02	1.05	0.74	7	0.5	0.83	0.92
	8		1.05	0.89	8		0.92	0.95

Source: own work.

adding a mixture of  $\text{CaCO}_3$  and  $\text{Ca}(\text{CH}_3\text{COO})_2$  to water, they dissociate. Calcium carbonate ( $\text{CaCO}_3$ ) has a relatively low solubility product ( $I_p = 8.7 \cdot 10^{-9}$  at  $25^\circ\text{C}$ ), and therefore, compared to the highly soluble calcium acetate –  $\text{Ca}(\text{CH}_3\text{COO})_2$ , it dissolves very slowly in water. Due to the fact that  $\text{Ca}(\text{CH}_3\text{COO})_2$  is a highly soluble substance, an increased concentration of  $\text{Ca}^{2+}$  is quickly formed in an aqueous solution, and water becomes saturated with these ions. The resulting  $\text{Ca}^{2+}$  reacts with  $\text{SO}_4^{2-}$ , resulting in the formation of a poorly soluble calcium sulphate salt ( $\text{CaSO}_4$ ), the solubility of which is  $0.2 \text{ g} \cdot \text{dm}^{-3}$  and which will settle at the bottom of the tank. Moreover, the dissociation products of the mixture of  $\text{CaCO}_3$  and  $\text{Ca}(\text{CH}_3\text{COO})_2$  will also be anions such as:  $\text{CH}_3\text{COO}^-$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ . Acetate ion ( $\text{CH}_3\text{COO}^-$ ) is not toxic, and its appearance in water in low concentration will not cause negative ecological effects on the environment. Acetate ions ( $\text{CH}_3\text{COO}^-$ ) undergo biological decomposition in water, while bicarbonate ions  $\text{HCO}_3^-$  and carbonate  $\text{CO}_3^{2-}$  ions formed in water will be used by taller plants as a source of carbon for photosynthesis. Therefore, as a result of precipitation of  $\text{SO}_4^{2-}$  in the form of poorly soluble  $\text{CaSO}_4$ , biological degradation of  $\text{CH}_3\text{COO}^-$  and the use of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  as a source of carbon for photosynthesis, the overall mineralisation of natural surface and mine waters is reduced.

## CONCLUSIONS

This work has shown that natural limestone can be effective in treating sulphate-containing, highly mineralised surface and mine waters. As experimental studies have shown, it is possible to increase the efficiency of extraction of sulphate ions by grinding it to  $1\text{--}10 \mu\text{m}$  and chemically modifying it with acetic acid. Prepared mixtures of crushed limestone and calcium acetate for research were taken in the proportions of  $\text{CaCO}_3:\text{Ca}(\text{CH}_3\text{COO})_2$  as  $1 : 1$ ,  $2 : 1$ ,  $3 : 1$  and  $4 : 1$ . The highest efficiency of extraction of sulphate ions ( $\text{SO}_4^{2-}$ ) was shown by a mixture of calcium salts taken in a ratio of  $1 : 1$ .

The analysis of various scientific studies allowed us to assume that when such a mixture of calcium salts is used to reduce  $\text{SO}_4^{2-}$  in natural surface waters, the formed acetate ion ( $\text{CH}_3\text{COO}^-$ ) will undergo biological degradation. Thus, it is possible to achieve a reduction in the total mineralisation of surface waters.

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### Authors' contributions

Conceptualisation: Y.T.; methodology: validation: Y.T. and R.T.; formal analysis: Y.T. and R.T.; investigation: Y.T. and R.T.; resources: Y.T.; data curation: Y.T.; writing – original draft preparation: Y.T.; writing – review

and editing: Y.T.; visualisation: Y.T. and R.T.; supervision: Y.T.; project administration: Y.T. and R.T.; funding acquisition: Y.T.

All authors have read and agreed to the published version of the manuscript.

## MOŻLIWOŚĆ ZASTOSOWANIA MIESZANKI SOLI WAPNIA W CELU ZMNIJSZENIA STĘŻENIA SIARCZANÓW ORAZ OGÓLNEJ MINERALIZACJI WÓD POWIERZCHNIOWYCH I KOPALNIANYCH

### STRESZCZENIE

Naturalny wapień może być wykorzystany do usuwania z wody siarczanów. Do wód mających wysoki poziom stężenia jonów siarczanowych należą wody powierzchniowe i kopalniane. W artykule przeprowadzono badania laboratoryjne z usuwania siarczanów z roztworów modelowych (pH 6–8) poprzez ich sorpcję i chemiczne wiązanie z solami wapnia. Do badań eksperymentalnych pobrano naturalny wapień, który został rozdrobniony do 1–10  $\mu\text{m}$ , następnie modyfikowano go kwasem octowym. Przeprowadzone w warunkach statycznych badania wykazały spadek stężenia siarczanów z 1,2 do 0,38  $\text{mg}\cdot\text{dm}^{-3}$  w ciągu 3 dni przy dodawaniu  $\text{CaCO}_3:\text{Ca}(\text{CH}_3\text{COO})_2$  w 1 : 1. Przeprowadzona analiza pozwoliła przypuszczać, że w przypadku zastosowania takiej mieszaniny soli wapnia do redukcji jonów siarczanowych w naturalnych wodach powierzchniowych powstały jon octanowy ulegnie biologicznej degradacji. W ten sposób możliwe jest osiągnięcie zmniejszonej całkowitej mineralizacji wód powierzchniowych.

**Słowa kluczowe:** siarczany, wody powierzchniowe, wapień, octan wapnia