



Sulphate Removal from Mining-Process Water by Capacitive Deionization

Maria SINCHE-GONZALEZ¹⁾, Raul MOLLEHUARA CANALES²⁾

¹⁾ University of Oulu, Oulu Mining School, P.O.Box 3000, FI-90014, Finland; email: maria.sinchegonzalez@oulu.fi

²⁾ University of Oulu, Oulu Mining School, P.O.Box 3000, FI-90014, Finland; email: raul.mollehuaracanales@oulu.fi

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Abstract

The removal of dissolved sulphate ions in water is one of the main challenges in the industry. Dissolved sulphate ions are ubiquitous in mining influenced waters because of its physical and chemical stability in aqueous solutions, including in process-water used by mineral beneficiation processes. It is a major problem for the mining industry because it can have negative impacts on the mineral beneficiation process and bring other issues for equipment and piping infrastructure. Not to mention the quality requirements for environmental water release. For instance, when water is recycled to the concentrator plant, dissolved sulphates can build up to increased concentration levels that can have negative effects in the processing of minerals.

This work proposes a new approach for the removal of sulphate ions from mining influenced waters, including process water, which is the capacitive deionization technique (CADI).

The technique can provide good quality water with low sulphate content suitable for recycling to the beneficiation process and meet adequate quality for recycling and safe release to the environment.

Synthetic process-water with sulphate concentrations similar to those in mining and mineral process water was prepared and treated by CADI at fixed conditions of electric current and residence time. The original sulphate concentration in water was 1000, 2000, 3000 mg/L; and reduction rates achieved of sulphate concentrations of 275 mg/L, 712 mg/L and 1015 mg/L, respectively. The results show effective removal of sulphate ions.

Keywords: water, sulphate, capacitive deionization

Introduction

This project aims to develop a new approach to remove sulphate ions from mining process-water by the CADI technique. The target is a low-sulphate water quality for utilisation and recycling in mineral processing, and for disposal into the environment.

Many industrial wastewaters, particularly those associated with mining operations and mineral processes contain high concentrations of sulphate ions exceeding quality standards for drinking water or ecological and biodiversity requirements. The water discharge in mining environments does not follow a uniform criterion because this is restricted to concentration limits based on ecological risk assessments and the sensitivity of the ecosystem receptors.

Table 1 shows permitted maximum sulphate concentrations for release in mining influenced waters in different jurisdictions. Countries with traditional mining activities can have sulphate concentration limits up to 1000 mg/L; but this is only a guideline. Environmental policies for water discharge depends on ecological risk assessments and water quality criteria for final uses.

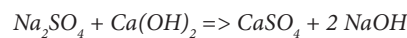
Sulphur-containing ions, particularly sulphate and thio-sulphate ions (Barskii et al., 1985) are present in the water of mining and mineral processing environments.

In mining and process recycled water, sulphate ions originate from the ore and reagents (Broman 1980) that accumulate in the liquid phase in appreciable concentration (>1500 mg/L). When the water is recycled, the concentration of sulphate can build up to high levels that may have an important harmful bearing on the mineral bene-

ficiation (Sinche et al., 2013), equipment, piping and to the environment.

Different ions react differently with sulphate, forming soluble and insoluble complexes (Silva et al. 2010) and may cause various kinds of problems in mineral treatment depending on concentration and associated species (Morris, Levy 1983) such as adsorption, depression, activation, others.

The most common method for removing high concentrations of sulphate from water is through the addition of hydrated lime ($\text{Ca}(\text{OH})_2$), which precipitates calcium sulphate:



Calcium sulphate hydrates to form the common mineral gypsum, which solubility is approximately 1467 mg/L as sulphate at 25°C. Sulphate reduction below 2000 mg/L has been possible in the past only through expensive technologies such as reverse osmosis (RO) or ion exchange (IX). RO and IX generate large volumes of liquid waste, which typically create additional treatment and disposal costs.

Capacitive Deionization – CADI

Capacitive deionization called desalination or electrochemical desalination is a relatively new method. It applies to water softening in seawater desalination and it is presented as a low-cost/low-energy, high yield method better than reverse osmosis (RO) and electrodialysis (ED) and with the advantage of removing all ionic contaminants (Weinstein, Dash 2013).

The technology is based on ion electrosorption at the surface of a pair of electrically charged electrodes, common-

Tab. 1. Recommended maximum sulphate levels (Ramachandran, 2012)
 Tab. 1. Rekomendowane poziomy maksymalne siarczanów (Ramachandran, 2012)

Authority	Sulphate Concentration (mg/L)
USA	500
Canada	1000
European Union	1000
South Africa	600
Australia	1000
World Health Organization (drinking water)	250

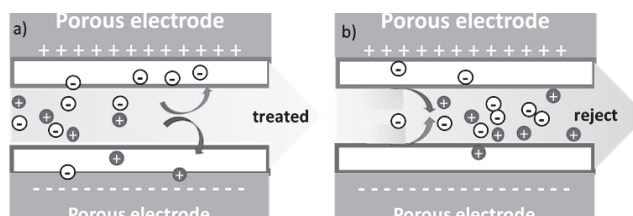


Fig. 1. Purification (a), Regeneration (b) stages in the capacitive deionization treatment
 Rys. 1. Fazy oczyszczania (a) i regeneracji (b) w procesie dejonizacji objętościowej

ly composed of highly porous carbon materials. It showed a wide range of capacities and it features real-time remote monitoring of pressure, flow, conductivity and desalination characteristics.

The water treatment has two stages purification and regeneration (Figure 1). In the stage of purification, the water passes between oppositely charged electrodes, which electrostatically remove dissolved ions, leaving pure water (treated) flowing out of the cell. The deionization cycle continues until the electrodes are saturated with ions. In the regeneration, the feed water flushed through the cell at a lower flow rate, while electrode polarity is reversed. Ions are ejected from the electrode surface, concentrated in the flow channel and slushed from the cell, producing a concentrate solution (reject) and electrodes are regenerated.

Materials and methods

Synthetic water

Mining influenced waters can contain large amounts of dissolved sulphate ions >1500 mg/l, and waters with less than 1000 mg/l are difficult for sulphate removal. Synthetic water containing 1000, 2000 and 3000 mg/L (Table 2) with and without interfering metal ions was prepared and used with the CADI treatment.

Ultrapure water and milliQ water, and reagents of analytical grade (i.e. CuSO_4 , NiSO_4 , ZnSO_4 , Na_2SO_4 , NaNO_3 , NH_4Cl , NaCl) were used to prepare synthetic water of various qualities for the research.

Capacitive Deionization – CADI tests

The tests were conducted in the Center of Technological Investigation of Water in the Desert-Ceitsaza, Chile.

The experimental work used a Capacitive Deionization equipment (Kit Model C-3-20FclFRG Voltea) with a 1.0 μm filter for pre-filtration (Figure 2). The Voltea program monitored and recorded in real time the experiments and experimental conditions as the equipment is logged for the entire duration of the experiments. The data was collected during

the experiments included a wide range of data on electric capacity, electric conductivity, electrical potential, cycle times, pressure, and flow. For every cycle, the average conductivity and voltage values were calculated.

Triplicate tests with synthetic water at various sulphate concentrations were conducted for reproducibility.

The capacitive deionization treatment relied upon the constant electricity operation. First, the water conductivity was measured and the sulphate removal percentage was set up by adjusting the residence time and outflows for the final streams (treated- and reject water). Treated water is the product water with low-sulphate concentration and the reject water is the residual brackish solution with high-sulphate concentration (Figure 3). The electric current in the cell is set up to a maximum of 60 Amperes (A) and the recovery of treated water is calculated in percentage as shown the Table 3.

Analysis of sulphate in water samples

Sampling and analysis were conducted on the feed, treated and reject waters. Sulphate determination was conducted by the gravimetric method with the ignition of residues. The method used hydrochloric acid (HCl) and barium chloride solution (BaCl_2) as reagents.

Results and discussion

Capacitive Deionization – CADI

The experimental work conducted several runs with varying conditions (i.e. removal rate, volume flow, retention time). Settings for the resultant treated – and reject waters were fixed as shown in Table 4 after measurement of the conductivity. The conductivity was 3.2, 3.22, 5.5 and 8.68 mS/cm for 1000, 2000 and 3000 mg/L of sulphate in synthetic water respectively.

The removal rate for water with a sulphate concentration of 1000 mg/L was 75%. A lower removal rate of 65% and longer retention time was required for water with a sulphate concentration of 2000 mg/L.

A 64% removal rate was achieved for a higher sulphate concentration of 3000 mg/L, but with a reduction in the re-

Tab. 2. Synthetic water at initial concentrations of 1000, 2000 and 3000 mg/L of sulphate, with interfering ions
 Tab. 2. Woda syntetyczna w początkowych stężeniach 1000, 2000 i 3000 mg/L siarczanu, z jonami przeszkadzającymi

Ions	Low without metal ions	Concentration, mg/l		
		Low	Medium	High
SO ₄ ²⁻	1000	1000	2000	3000
NO ₃ ⁻	20	20	40	60
Cl ^{-*}	100	100	200	300
Cu ²⁺		2	5	8
Ni ²⁺		2	5	8
Zn ²⁺		5	10	15
NH ₄ ⁺		10	20	30

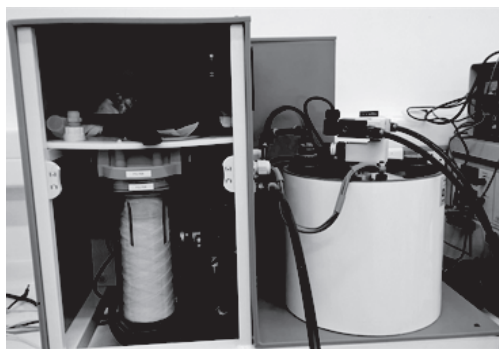


Fig. 2. Capacitive Deionization equipment (Ceitsaza, Chile)
 Rys. 2. Sprzęt do dejonizacji objętościowej (Ceitsaza, Chile)

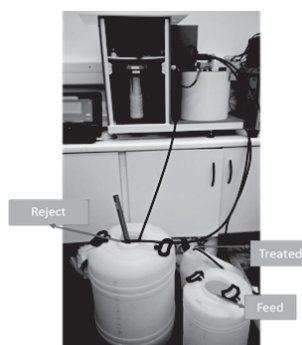


Fig. 3. Feed, treated and reject solutions from the CADI treatment
 Rys. 3. Nadawa, produkty i odpady z procesu CADI

tention time and the volume flows (treated water from 1 to 0.65 L/min; reject water from ~0.4 to 0.2 L/min). The experiment attempted higher electric current values but this was not possible as the values exceeded the capacity of the equipment.

A higher sulphate removal rate was obtained in the absence of interfering ions such as Cu, Ni, Zn in the water. The test was carried out for a low-sulphate concentration only (1000 mg/L), with a removal rate of 80%.

The result using the CADI method should be interpreted not only in terms of sulphate removal rates but also in terms of the final products that is the amount of water treated in a continuous flow (treated water and reject water).

Table 5 presents the results for effective removals and volume recoveries. The reconciled volume flow in the feed water (1.47 L/min) was maintained constant. Maximum volume recovery was achieved from low-sulphate concentration water (1000mg/L) in absence of interfering ions, resulting in 77% water recovery (1.13 out of 1.47 L/min), and 80% sulphate

removal rate (1000 to 200 mg/L). In the presence of interfering ions, the water recovery is similar (1.16 L/m), but the sulphate removal decreases to 75% (250 mg/L). For synthetic water with a sulphate concentration of 2000 mg/L, the water recovery is 68% (1 L/min) but the removal rate decreases to 65% (2000 to 700 mg/L). For higher concentration of sulphate (3000 mg/L), the recovery rate is 70% (1.03 L/min), with only 64% of sulphate removal (3000 to 1080 mg/L).

The results show that the CADI method can achieve water volume recoveries in the range of 68–79% in a wide range of sulphate concentrations (1000–3000 mg/L) in water. However, the resulting brackish solution or reject water requires further investigation for treatment. In Chile, the alternative is the natural solar evaporation as in the treatment of brines with potential sulphur recovery.

In the case of water with 3000 mg/L of sulphate, the reduction is to 1080 mg/L. A secondary treatment stage could further reduce the concentration levels and increase the recovery rate to at least 75% (as for the case of synthetic water

Tab. 3. Setting up the variables for calculation of current and recovery of the treated water. Feed water 2000 mg/L, conductivity 5.50 mS/cm
 Tab. 3. Ustawienie zmiennych dla obliczenia napięcia i odzysku wody procesowej. Woda w nadawie 2000 mg/L, przewodność 5,50 mS/cm

Constant Current Operation					
Settings Calculator					
Adjustable Settings			Calculated Settings		
Conductivity	5.5	mS/cm	Treated Current	59.5	A
Removal	65	%	Reject Current	60	A
PreTreated Flow	1	l/min			
Treated Flow	1	l/min	Recovery	68	%
Reject Flow	0.4	l/min			
PreTreated Time	5	sec			
Treated Time	115	sec			
Reject Time	125	sec			

Tab. 4. Setting the conditions to treated water with different concentrations
 Tab. 4. Ustalenie warunków dla wody procesowej o różnych koncentracjach

Ions	Units	Water with Sulphate			
		Low	Medium	High	Low (not metals)
SO ₄ ²⁻	mg/L	1000	2000	3000	1000
Conductivity	mS/cm	3.22	5.5	8.68	3.2
Removal	%	75	65	64	80
PreTreated flow	L/min	1.0	1.0	0.65	0.9
Treated flow	L/min	1.0	1.0	0.65	0.9
Reject flow	L/min	0.3	0.4	0.2	0.3
PreTreated time	sec	5.0	5.0	5.0	5.0
Treated time	sec	110	115	64	110
Reject time	sec	82	125	70	82
Treated current	A	40.3	59.5	60.1	38.7
Reject current	A	59.4	60.0	59.5	57.0
Recovery	%	79	68	70	77

Tab. 5. Calculated water recovery and sulphate removal
 Tab. 5. Obliczony uzysk wody i stopień usunięcia siarczanów

Ions	Units	Water with Sulphate			
		Low	Medium	High	Low not metals
SO ₄ ²⁻	mg/L	1000	2000	3000	1000
Reconciled feed to maximum flow treated	L/min	1.47	1.47	1.47	1.47
Recovery	%	79	68	70	77
Treated flow	L/min	1.16	1.00	1.03	1.13
Removal	%	75	65	64	80
Final sulphate in treated, calculated	mg/L	250	700	1080	200
Concentrate flow, calculated	L/min	0.31	0.47	0.44	0.34

Tab. 6. Summary of various sulphate concentration in synthetic water treated (calculated and analysed)
 Tab. 6. Podsumowanie różnych koncentracji siarczanów w sztucznej wodzie procesowej (obliczone i empiryczne)

Calculated	Analysed SO ₄ (mg/L)			pH			Conductivity
	Feed	Treated	Reject	Feed	Treated	Reject	
SO ₄ (mg/L)							mS/cm
1000	1073	275	3041	8.18	9.73	8.12	3.22
2000	1925	712	3706	6.98	7.37	6.58	5.5
3000	3008	1015	5354	6.18	6.63	6.24	8.68

with 1000 mg/L). This requires additional investigations to evaluate the technical and economic pros and cons.

Results of sulphate concentration in the feed, treated and reject waters are shown in Table 6, which is comparable with the calculated values from Table 5. In addition, the chemical analysis of the sample shows a good correlation with the calculated amounts of reagents required to prepare the synthetic waters (~1.3% difference). It is also observed

that the removal of sulphate resulted in an increase of the pH (~ 1 unit) which is also an indication of reduction of the acidity.

Figure 4 shows the concentration in the feed and in the products (treated and reject) after treatment. Results show a linear trend for the three solutions indicating that removal rates are proportional to concentrations of sulphate in the feed.

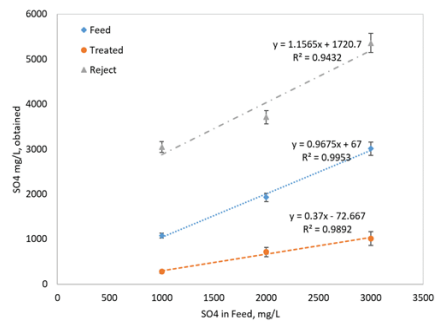


Fig. 4. Chemical analysis of sulphate concentration in synthetic water before and after treatment
 Rys. 4. Analiza chemiczna stężenia siarczanów w sztucznej wodzie procesowej przed i po procesie

Conclusions

Capacitive deionization is an alternative treatment option for sulphate containing waters.

The advantage of the technique is its capacity for a continuous flow treatment process.

Capacitive deionization shows to decrease sulphate ions from a wide range of concentration solutions.

Capacitive deionization proved to yield higher recovery rates compared to RO that has a recovery rate of 50% or less. The technique is of low power consumption and uses only 0.5 KWhr/m³ of treated water.

Synthetic water with similar concentration to those found in process and mining water were tested. The use of real pro-

cess-water is the next step to evaluate the technique. The challenge, in this case, is the presence of solids in suspension and fines particles.

The testing technique in this work generated a residue called here as reject water, which requires further investigation to handle it.

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Usuwanie siarczanów z wody procesowej za pomocą dejonizacji pojemnościowej

Usuwanie uwolnionych jonów siarczanowych w wodzie jest jednym z głównych wyzwań w przemyśle. Uwolnione jony siarczanowe są wszechobecne w wodach będących pod wpływem działań górniczych ze względu na ich fizyczną i chemiczną stabilność w roztworach wodnych, wliczając w to wody procesowe stosowane podczas procesów wzbogacania. Jest to główny problem dla przemysłu górniczego ponieważ ma to negatywny wpływ na proces wzbogacania oraz powodować może także problemy sprzętowe i infrastruktury rurowej. Ponadto, nie należy zapominać o wpływie takiej wody na środowisko naturalne. Dla przykładu, kiedy woda jest kierowana do procesów przerobczych, uwolnione siarczany mogą się namnażać do poziomów wysokiej koncentracji a to ma negatywny wpływ na prowadzone procesy. Praca ta proponuje nowe podejście do problemu usuwania jonów siarczanowych z przemysłowych wód górniczych, wliczając w to wody procesowe, którym jest zastosowanie dejonizacji pojemnościowej. Technika ta daje dobrej jakości wodę o niskiej zawartości siarczanów, która jest odpowiednia dla procesów wzbogacania i jest zgodna z wymogami jakościowymi dla recyklingu a tym samym bezpieczna dla środowiska naturalnego. Sztuczna woda procesowa o zawartości siarczanów podobnej do wody przemysłowej z zakładów przerobczych sektora górniczego została przygotowana i poddana procesowi CADI w stałych warunkach napięcia elektrycznego i czasu. Oryginalna koncentracja siarczanów w wodzie wynosiła 1000, 2000, 3000 mg/L a stopień redukcji osiągnięty wyniósł, odpowiednio, 275 mg/L, 712 mg/L oraz 1015 mg/L. Wyniki pokazały efektywność w usuwaniu jonów siarczanowych z wody procesowej.

Słowa kluczowe: woda, siarczan, dejonizacja objętościowa