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The Development Of A Treatment Process For The Mine Water Containing Arsenic And Thiocyanate From Lab Scale To Pilot Plant Scale.

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Abstract

About 8 million metric tons storage of cyanidation tailings from a former French gold mine produces a 10 m³/h mine drainage that contains around 8 mg/L of As and 1 g/L of SCN⁻ and is currently treated with a lime process. The existing treatment plant produces large amounts of sludge reflecting the large amounts of sulfate present in water and calcium from lime. The present study aims to developing a semi-passive mine water treatment process that would produce a lower amount of sludge and improve the treatment efficiency with a target discharge level under 100 µg/L of Arsenic.

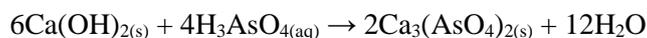
Introduction

As a first step, several options have been considered for arsenic and thiocyanate treatment whilst taking account the mine water characteristics.

Arsenic treatment:

Nowadays, arsenic treatment processes can be classified into four categories (Vu, 2003): Ion exchange, Membrane processes, Precipitation or Adsorption. Ion exchange and membrane processes have been excluded due to their cost and low efficiency. Precipitation can take place in acidic conditions, e.g. the precipitation of arsenic with sulphide forms Orpiment (As₂S₃) or Realgar (As₄S₄). As a real example, a large-scale precipitation bioassay has been implemented for heavily loaded arsenic (200 mg/L) water at the Trail site (British Columbia, Canada) (Evans, 2011). The pH of treated water rose from 5.8 initially to 6.5 and the arsenic concentration was reduced to 0.75 mg/L.

The lime treatment of arsenic waters is a precipitation process and has commonly been used in metallurgical production units (Riveros, 2001). Arsenic (V) co-precipitates to give calcium arsenate according to:



This process generates large amounts of contaminated sludge, potentially able to release arsenic with time, thus it is not efficient at long term.

An alternative is the adsorption of arsenic on oxides of manganese (Hou 2017, Mishra 2016), aluminum or iron, and this has been widely studied to treat arsenic waters (Kaminski 2003) or on lanthanum compounds (Tokunaga, 1997, Haron 2001). At pH < 7.5, As (V) is more easily trapped than As (III). Concerning the adsorption of arsenic, several competing anions are identified: carbonates, bicarbonates and phosphates ions (Burnol 2007). Competition occurs mainly at low pH around 6. At pH 8 competition appears very limited (Burnol 2007). Finally, pH can limit adsorption of arsenate if pH is larger than 8 (Raven 1998).

Thiocyanate treatment:

Thiocyanate can be treated by chemical processes with strong oxidants like ozone or hydrogen peroxide (Gould 2012). However, these chemical processes are either ineffective, or too expensive, or generate one or more hazardous by-products, so they are usually not implemented in practice. Thiocyanate can advantageously be removed by bio-processes, based on its oxidation catalyzed by bacteria that use them as energy, sulfur, carbon and nitrogen sources. Some mining sites use this process at the industrial scale, such as the gold Homestake mine (South Dakota, United States) (Mudder 1984) and the Nickel Plate mine (British Columbia, Canada) (Gould 2012). Different technologies for enhancing contact between bacteria and water can be used: simply agitated continuous reactors (suspended bacteria), ascending biofilters, trickle biofilters, fluidized supported beds. These are essentially active technologies whose kinetics of degradation of thiocyanates range between 15 mg SCN⁻ /L/h (Villemur 2015) and 194 mg SCN⁻ /L/h (Jeong 2006).

After considering potential processes used for arsenic and thiocyanate removal, the process retained here is based on the adsorption of arsenic on ferrihydrite precipitate combined with the biodegradation of SCN⁻. In the present study, a semi-passive mine water treatment process is developed, in order to

produce a lower amount of sludge and to improve the treatment efficiency (target discharge level under 100 µg/L of Arsenic).

Background

Water pollution caused by mine drainage is a modern concern that requires to be addressed in order to protect local ecosystems and fulfill the regulation. This study focuses on treatment of cyanide (CN⁻), its derivate thiocyanate (SCN⁻) and arsenic (As) in a water drainage originating from mine tailings of a former gold-mine site. In this site, 10 m³/h (average) of water is produced by around 8 million metric tons storage of cyanidation residue. This water contains around 8 mg/L of As and 1 g/L of SCN⁻, is rich in dissolved salts (Table 1) and has a pH close to 8. This water is currently treated within a lime process. The treatment plant produces large amounts of solid waste (sludge), mainly calcite (CaCO₃), gypsum (CaSO₄), and brucite (Mg(OH)₂), reflecting the large amounts of sulfate present in water and the amounts of lime used in process.

Table 1: Overall composition of contaminated water. Elements with concentration below 0.1 ppm are not shown, namely: Ag, Al, Au, Ba, Bi, Br, CO₃²⁻, Cd, Cr, Cu, Co, NO_{2,3}, Pb, Sb, Sn, Zn.

Substance	Conc. (mg/L)	Substance	Conc. (mg/L)	Substance	Conc. (mg/L)
SO ₄ ²⁻	7 800	Mg ²⁺	180	Total cyanide*	1.30
Na ⁺	2 500	K ⁺	110	Sr	1.30
SCN ⁻	1 000	As	7.50	Mn	1.20
Ca ²⁺	450	Si	6.07	F	1.00
HCO ₃ ⁻	250	PO ₄ ³⁻	4.50	NH ₄ ⁺	0.25
Cl ⁻	200	Fe (total)	1.00	B	0.10

*thiocyanate SCN excluded

In the lime process, arsenic is trapped as calcium arsenate. Process efficiency reaches 90 % on average, the outlet concentration being between 0.5 mg/L and 1 mg/L of arsenic when regulatory objective is generally 0.1 mg/L in discharge waters. However, calcium arsenate is an unstable product that reacts with atmospheric CO₂ to form soluble arsenic and calcite (Riveros, 2001). In addition, the current process does not remove thiocyanate from effluent. Instability of calcium arsenate, the large quantities of sludge produced and high operating cost of lime process brought the post-mining department (DPSM) of BRGM (the French geological survey, in charge of the site since 2006) to look for a more efficient process. This work implied lab experiments that ultimately aimed at designing an on-site pilot plant.

Lab experiments

In order to develop a pilot plant on-site, numerous lab experiments were performed: batch experiments, followed by continuous lab experiment with columns filled with pozzolana for both thiocyanate bio-oxidation and arsenic adsorption, and finally continuous lab experiments in which columns were replaced by a settling tank for arsenic adsorption and co-precipitation with iron.

First, batch experiments aimed to determine the optimal iron concentration (10 to 30 mg/L) and to test the relative efficiency of two sources of Fe III: Fe II sulfate (that is rapidly oxidized into Fe III) and Fe III chloride. **Figure 1** shows results of this batch experiment. It is noticed that FeIII reacts faster than FeII. A few minutes are enough to reduce arsenic concentration. Nevertheless, FeII sulfate appears more efficient than FeIII chloride as it prevents the late release of arsenic after 24 h (**figure 1**).

Continuous lab experiments consisted in mixing ferrous sulfate solution (Fe²⁺ 20 mg/L) with contaminated water flow of 10 mL/h through a bio-filter column made of pozzolana (working volume of 300 mL) which represented a residence time of 30 hours. Moreover, due to an injected airflow of 100 mL/min in order to supply O₂ for iron-oxidizing bacteria, the column behaves as a continuous stirred tank reactor. Bio-oxidized iron precipitates as iron hydroxide (ferrihydrite) presenting numerous adsorption sites readily available for arsenic adsorption. **Figure 2a** shows that 98 % of arsenic removal

was then achieved, reaching below 100 $\mu\text{g/L}$ in the outlet, which is the acceptable limit for arsenic-bearing effluent discharge in the environment. A second experiment (**figure 2b**) was conducted with a contaminated water flow of 21.5 mL/h in order to measure the adsorption kinetics of arsenic. The column could remove 0.141 mg of arsenic per hour, which represents a rate of 0.47 mg/L/h.

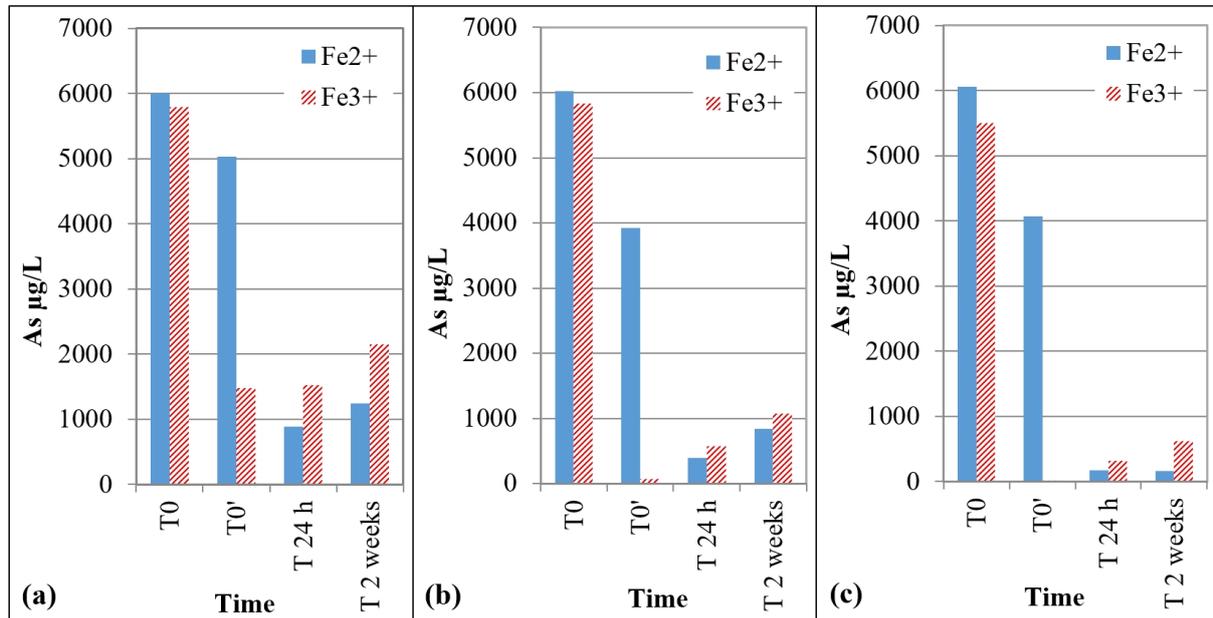


Figure 1 Batch experiment results with respectively 10 (a), 20 (b) and 30 (c) mg/L of Fe II and Fe III.

In order to improve the process and to optimize operational cost of the already satisfying lab-scaled process, a simpler process was tested. It consists of mixing iron and contaminated water in a tube before injecting it in a longitudinal settling tank ($S=440\text{ cm}^2$, $V=1450\text{ mL}$). The inlet contaminated drainage water flow is 21.5 mL/h. Residence time distribution was assessed and an average residence time of 67.2 h was determined. After 5 days of continuous operation, a significant amount of arsenic was trapped into the ferrihydrite sludge.

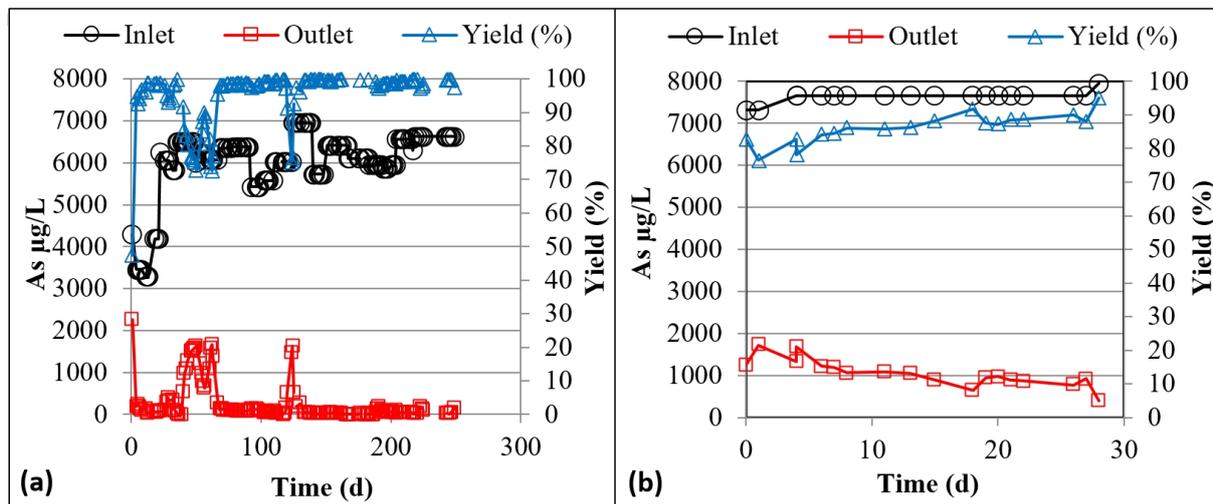


Figure 2 Performance of the pozzolana column with addition of iron sulfate 20 mg/L: (a) treating 10 mL/h of arsenic water; (b) treating 21.5 mL/h of arsenic water.

Complete oxidation of ferrous iron was achieved and the effluent contained 2 mg/L of arsenic, indicating a 70 % arsenic removal (**figure 3a**). Arsenic was present in soluble form (filtration at 0.45 μm) (50 % of total As) and in particles form associated to iron oxides which were formed in the settling tank. A second experiment was conducted on settling tank (**figure 3b**), with a contaminated flow of 55 mL/h representing a residence time of 34.7 h and an input iron concentration of 25 mg/L. The goal was to enhance the sedimentation of particles via higher iron concentrations. Results (**figure 3b**) show a lower concentration of dissolved arsenic (300 $\mu\text{g/L}$ average) in the effluent but it remains always around

2 mg/L of arsenic adsorbed on iron hydroxide particles. In conclusion, it is efficient and allows to reduce soluble arsenic concentration by 96 %. This step should be followed by a filtering step to remove the iron particles and meet the target discharge level of 100 µg/L. Regarding thiocyanate biodegradation, two bioreactors were implemented. Bio-oxidation of SCN⁻ was carried out in an aerated pozzolana bio-filter column functioning in a recycling mode in order to be in “batch” reactor conditions. Reaction rate was monitored over several batches. The first reactor had 440 mL of effective volume while the second had 3000 mL. The airflow was 100 mL/min for the first column and 1 L/min for the second one. The model reaction is the following:

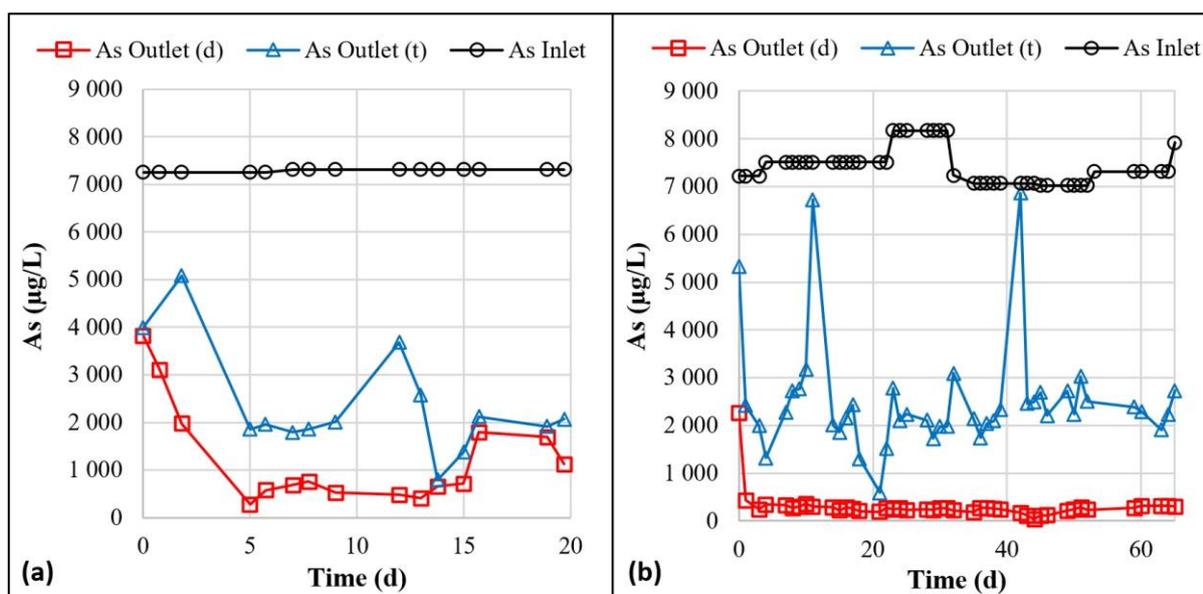
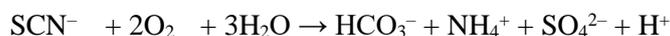


Figure 3 Performance of settling tank: (a) with addition of iron sulfate 20 mg/L and residence time of 67 h ; (b) with addition of iron sulfate 25 mg/L and residence time of 34.7 h.

Thiocyanate concentration effectively decreased from 1000 mg/L to below quantification limit in approximately 12 days (**figure 4a**). A linear degradation rate of -4.5 ± 1 mg/L/h was observed repeatedly. **Figure 4b** shows results obtained when the column was switched in continuous mode. A -2.5 mg/L/h degradation rate was then observed. Dictor (1997) reached 81 mg/L/h over the course of 6 months of optimization. The short duration of the experiments could explain the observed low degradation rate. The lack of biofilm development is suspected to be the major factor limiting the degradation rate. At the end of batch experiments, ammonium was quantified in significant proportions (half of the initial quantity of SCN) whereas nitrate remained under quantification limit.

Design of the pilot plant for on-site experiments.

An on-site experiment will be carried out in order to complement key data before final upscaling. According to lab scale experiments results, pilot plant will consist of two treatment steps. The pilot plant will treat a contaminated water flow of 0.100 m³/h. In a first step, thiocyanate will be treated in a biofilter. According to the degradation rate found in literature (Dictor, 1997), a working volume of 1.3 m³ is needed. Given the pozzolana porosity (40%), a 3 m³ biofilter volume will be implemented. A second treatment step will consist in adsorption of arsenic on iron hydroxide and precipitate separation with a settling tank followed by a pozzolana filter to remove particles. According to lab scale experiments, a minimum settling tank volume was estimated at 1.7 m³. We designed a settling tank unit, consisting of a mixing chamber of 0.1 m³ separated by a baffle from a 3.3 m³ settling tank which allows to accumulate sludge during time. This settling tank is followed by a finishing pozzolana filter of 0.9 m³. –The process flow diagram in **figure 5** illustrates the operations conducted to treat a 0.100 m³/h flow. A buffer tank upstream will allow passive flow of water through the whole process.

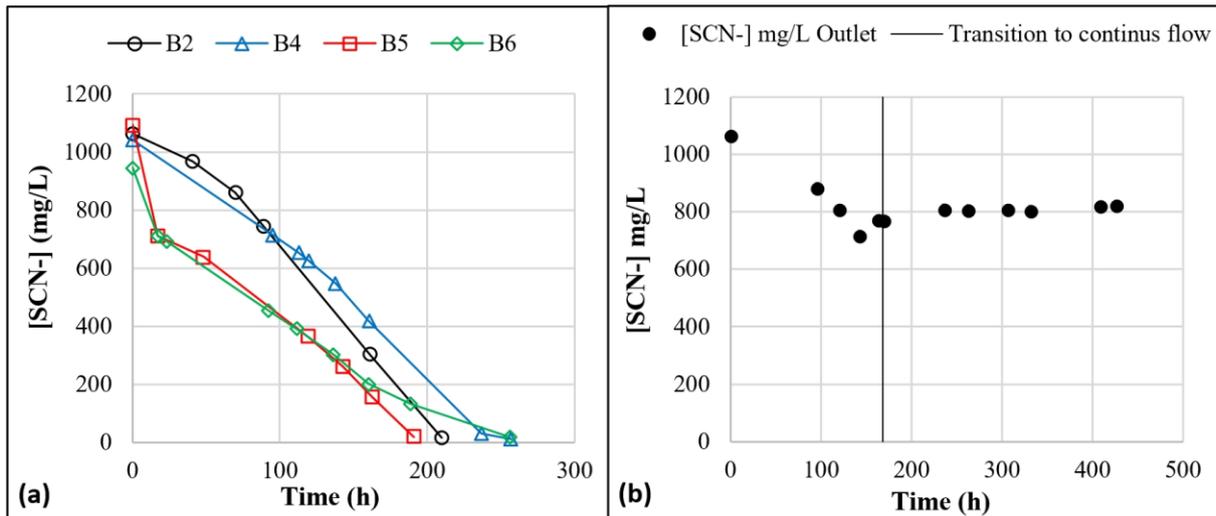


Figure 4 Thiocyanate degradation on pozzolana column; (a) Batch experiments; (b) Continuous flow experiment.

Pilot monitoring program

Pilot experiment will be performed during at least one year, in order to undergo the different weather conditions of the four seasons. Key-parameters to be monitored and evaluated include clogging of biofilters, temperature, and rainfall dilution. A regular monitoring of arsenic oxidation state during operations (as III or V) will also be important for the understanding of process performance, as laboratory experiments did not use freshly drained water. Evolution of thiocyanate degradation rate will be also a key parameter to follow, an increase of degradation rate being expected over time. Iron sulfate concentration should be finely optimized at pilot scale. Feeding modes (bottom up flow and down-flow) will be compared to determine their impact on clogging. Finally, on-site pilot could be an opportunity to identify the potential operational problems due to on-site environmental factors such as algae formation or undesired bacterial contamination.

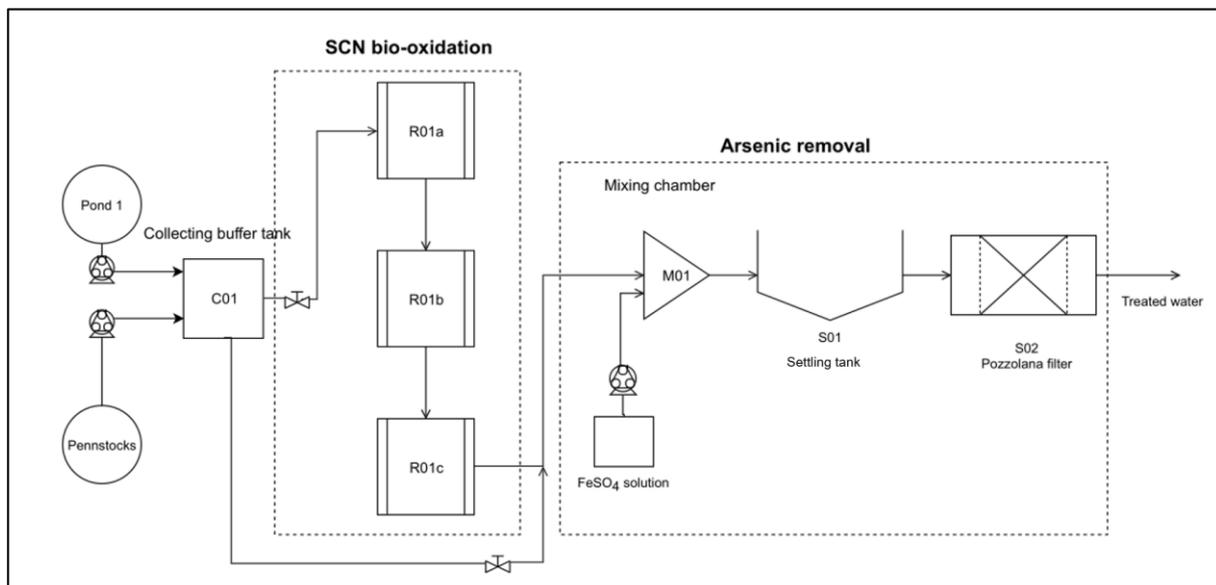


Figure 5 Process flow diagram of on-site pilot experiment.

Conclusion

This study was conducted in order to develop and build an optimized mine water treatment plant that will replace the current lime treatment plant. The goal is to develop a more efficient (reduced amount of sludge) and cost effective process. In order to achieve this goal, lab scale experiments were conducted and key data for process upscaling were obtained for the treatment of a mine water containing arsenic and thiocyanate.

As first results, this approach allowed us to design a treatment process for a contaminated mine water with its own characteristics. An in-situ pilot plant was designed. Pilot plant experiments will be conducted from first semester 2019. Key parameters will be followed and the impact of climate variability (temperature) and rainfall will be assessed. This “pilot plant” step must allow to design a treatment plant that will be as much as possible passive. For example, passive oxygenation could be achieved by taking advantage of the site slope using waterfalls. Only pumping of water and injecting ferrous sulfate solution will need energy.

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