Electrolytic salt splitting for sulfuric acid and caustic recovery: can it be cost-effective?

Alexander Burns and Clive Brereton

Abstract Electrolytic salt splitting is a technology where acid and/or base is regenerated from a neutral salt using membrane electrolysis. Recent advances in the understanding of brine treatment, membrane stability, and cell design have made electrolytic salt splitting feasible on certain hydrometallurgical solutions. Meanwhile, environmental regulations have made the bulk disposal of salt solutions more difficult. In this paper, sodium sulfate salt splitting is examined from a cost perspective, compared to purchasing the reagents directly. Relative costs are estimated for several regions based on published electricity and reagent prices. The results show that salt splitting is economically favourable in some regions, and can be made more favourable by applying modifications to the traditional three-compartment design.

1 Introduction

Waste salt solutions are common in hydrometallurgical processes. Sodium sulfate, for example, is generated by neutralizing sulfuric acid with caustic. Electrolytic salt splitting can be used to regenerate acid and base from such solutions, which can then be reused elsewhere in the plant, such as for leaching, neutralization, IX elution, or SX stripping. This establishes a closed loop system that can dramatically reduce net reagent consumption and water usage, while eliminating the need to dispose of large quantities of a salt. Central to the technology is the electrolytic cell stack, an example of which is shown in Figure 1.

The technology for salt splitting of neutral salts dates back to before 2000. For example, Velin compared technologies for 3- and 4-compartment sodium sulphate salt splitting in 1999 using a cell with 4 x 0.5 m^2 membrane area (Velin (1999)). Though salt splitting from barren effluents is not currently practiced in the mining industry, variations are in use or have been proposed at other points in the production process. Lithium sulfate solutions may be electrolytically split into lithium hydroxide and sulfuric acid, as is described in the patent literature (Brown (1977); Retallack (1981); Magnan et al (2016). Lithium sulfate salt splitting is currently practiced by Nemaska at their demonstration plant in Shawinigan, Quebec, and is in development for Pure Energy's lithium brine resource in Nevada using technology developed by Tenova (Nem (2016); Pur (2017)). NeoMetals's ELi process operates under similar principals, but in the chloride system (Eli (2018)). The Electrosynthesis Company and Ormiston Mining and Smelting Co. developed a process to split sodium sulfate, improving the current efficiency by continually neutralizing the anolyte with ammonia, producing ammonium sulfate and caustic (Genders et al (1994)). Membrane electrolysis processes have been demonstrated for the recovery of hydrochloric acid from spent pickling solutions in steel mills (Regel-Rosocka (2010)).

The technical and economic drivers relevant to salt splitting are different at each site, and depend on process chemistry, electricity prices, reagent prices, water use restrictions, environmental regulations, and other site-specific concerns. In this paper, a cost model was developed for an electrolytic salt splitting cell house. The model was then

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applied to various site locations around the world based on published electricity and reagent prices. Though not covered here, the same analysis techniques could be applied to other chemistries and locations when investigating the economic feasibility at specific sites.
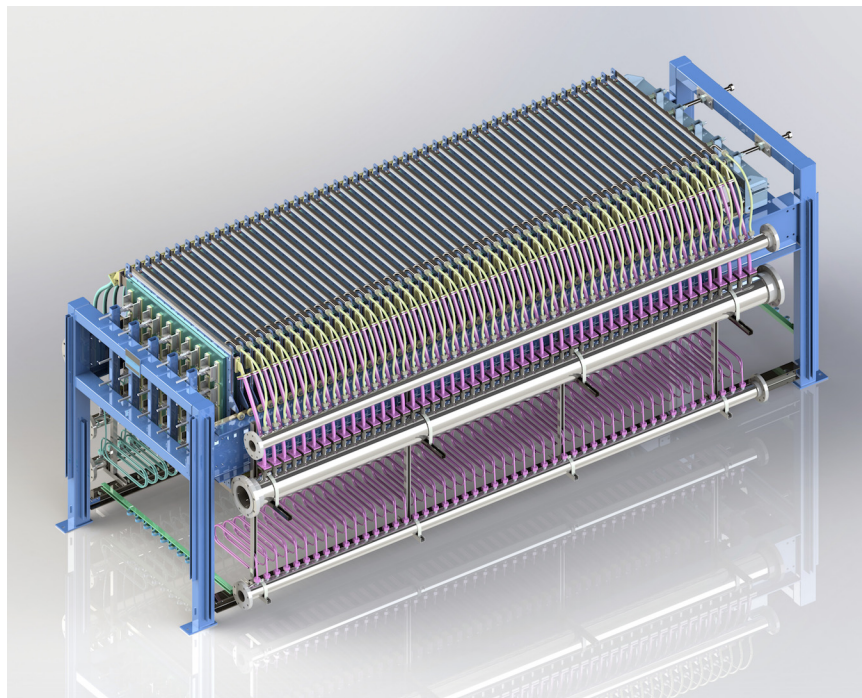

Fig. 1 NorScand cell stack, 3-compartment salt splitting configuration. 50 cell carriage, $1.5\,\mathrm{m}^2$ per cell.

2 What is electrolytic salt splitting?

Electrolytic salt splitting is a technology that uses an applied electric potential and one or more ion selective membrane(s) to regenerate an acid and a base from a salt solution. A variety of cell configurations can be used, depending on the desired product (acid, base, or both), the required product strength, and the types of membranes compatible with the solution. There are three general classes of membranes in use for salt splitting. Cation exchange membranes (CEM) preferentially pass positively-charged ions (e.g. sodium) to balance charge. Anion exchange membranes (AEM) preferentially pass anions (e.g. sulfate) to balance charge. Bipolar membranes are effectively a laminate of both, and rely on the splitting of water at the interface between the two to balance charge. Three different cell configurations, applied to splitting a sodium sulfate stream, are shown in Figure 2: a three-compartment cell, a two-compartment cell, and a bipolar membrane electrodialysis (BME) cell.

The main design equation is Faraday's Law of Electrolysis:

$$\dot{m} = \eta_{\mathrm{m}} \frac{jAM}{zF} \tag{1}$$

where $\dot{m}$ is the mass transfer rate of the target ion across the membrane $(\mathrm{g\,s}^{-1})$, j is the superficial current density $(\mathrm{A\,m}^{-2})$, A is the total superficial electrode area (m^2), M and z are the molecular weight $(\mathrm{g\,mol}^{-1})$ and charge of the species being transferred across the membrane, F is Faraday's constant $(96485\,\mathrm{C\,mol}^{-1})$, and η_{m} is the membrane transport current efficiency, which is defined as the fraction of the total current that acts to transfer the target ion (e.g. Na^+) across the membrane. Note that the equation differs slightly from the familiar form used for other applications (e.g. electrowinning) because in this case it is formulated to account for ion transport across the membrane, rather than work done at the electrode.

For a multi-compartment electrolysis cell, it is worth noting that the current efficiencies across the various membranes may all be different. This is because factors such as back-migration of counter-ions and other factors will be different on the anodic and cathodic sides. Also, η_m can vary with current density, solution composition, temperature, membrane age, and other factors. The reasons for this are beyond the scope of this paper, but suffice to say, with novel chemistries it is typically necessary to measure η_m in the laboratory.

The current efficiency of a salt splitting cell generally improves at higher brine concentration and lower product concentrations. If required, the products can be strengthened in a subsequent operation (e.g. evaporation). The optimal operating point is a balance between the power consumption of the cell house, the needs of downstream users, and the restrictions of the cell technology. For example, 3-compartment electrolysis systems may be readily designed for up to 20 wt. % NaOH in the anolyte, but many BME systems are efficient only to 5-10 wt. %.

Salt splitting flow sheets are typically an optimized combination of water management (e.g. evaporation or R.O.), electrolysis, and careful brine treatment to promote long membrane life. Often the most problematic impurities from the perspective of membrane fouling are the alkaline earth metals (Mg, Ca), which must be removed in a brine treatment step prior to electrolysis. Other impurities may affect the process to a lesser degree.

Salt splitting is not restricted to sodium sulfate; it can also be used in the chloride or nitric systems, in combination with electrowinning, or as an enabling technology for other, novel processes, such as the co-production of ammonium sulfate (which can be sold as fertilizer) or for the purification and recovery of lithium.

3 Plant design and operating conditions

A flow sheet for a typical cell house is shown in Figure 3. The following equipment is standard:

Cell stacks: Banks of cells arranged hydraulically and electrically in a series and/or parallel configuration. Hundreds or thousands of m^2 of active cell area may be required, depending on the production rate. A salt splitting cell house typically operates between 30 °C to 70 °C and <1 barg, which may simplify materials of construction compared to some other membrane electrolysis systems, such as those used in a chloralkali plant.

Transformers/rectifiers: Converts AC power to DC.

Circulation pumps and tanks: Tanks and pumps for each cell compartment. These can be operated continuously using a feed/bleed arrangement or in batch, depending on the process. Water may be added to the circulation loops to maintain the water balance.

Coolers: Remove heat to maintain the desired operating temperature.

Liquid distribution piping and manifolds: Branched piping serves to distribute flow from the circulation tanks to the cells. It is also designed to perform gas disengagement and minimize shunt current losses.

Gas handling: Piping and instruments to safely handle hydrogen and oxygen. These gases can be compressed and used elsewhere in the plant, if desired.

Brine treatment: Pre-treatment of electrolytes to remove impurities harmful to the membranes, such as Ca and Mg.

Product and brine concentration: Evaporator, crystallizer, reverse osmosis, or other technology to further concentrate the electrolyte streams. This is required in order to achieve the concentrations required for a recyclable or salable product, and to maintain the water balance of the system.

4 Operating cost

Electrical energy

In most cases, the largest operating cost is electrical power, which is calculated as follows:

$$P_{AC} = V j A \eta_p \tag{2}$$

where P_{AC} is AC power consumption (kW), V is the applied cell potential (DC), j is the superficial current density (A m^{-2}), A is the total superficial cell area (m^2), and η_p is the overall power efficiency, including AC to DC conversion and bus losses.

a) 3-compartment electrolysis cell.

b) 2-compartment electrolysis cell.

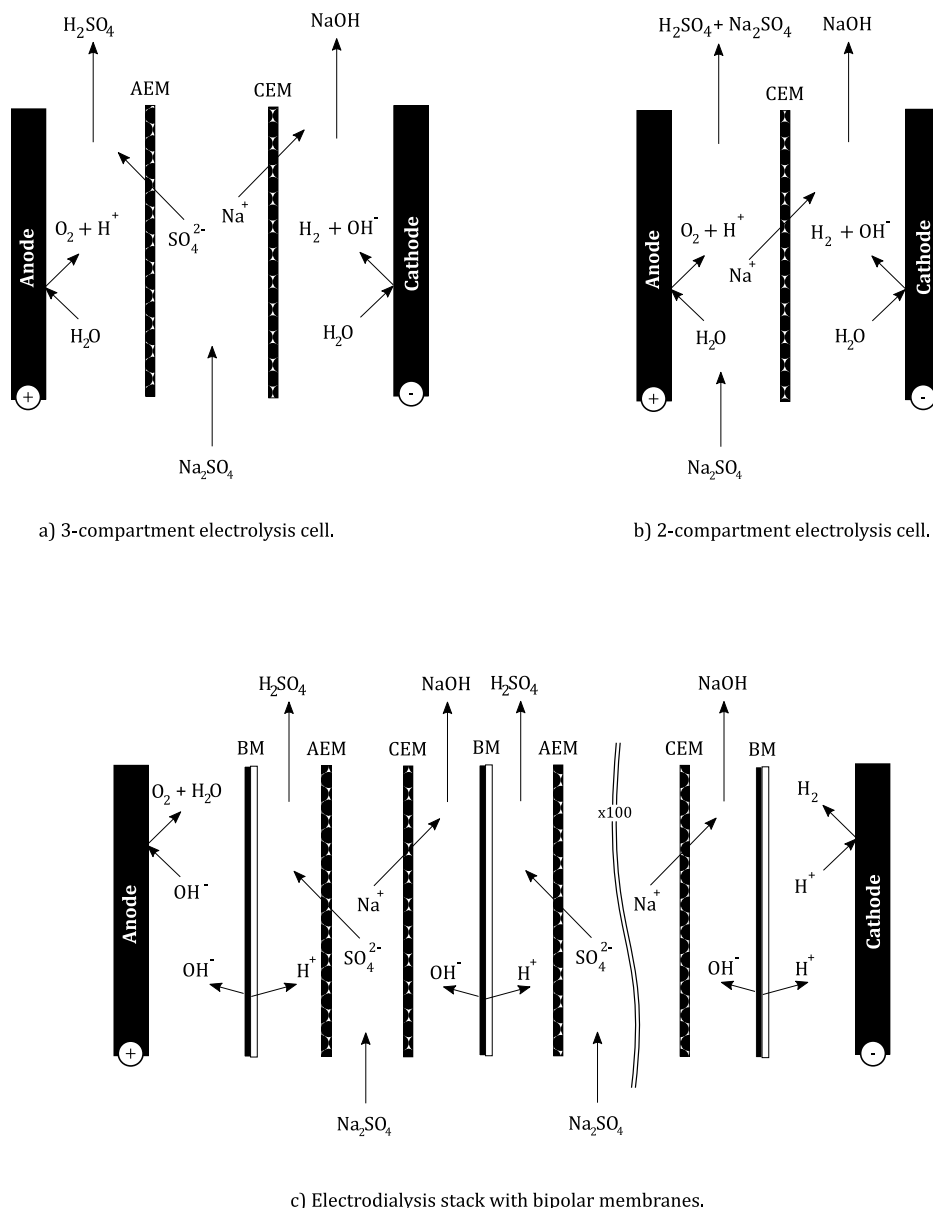c) Electrodialysis stack with bipolar membranes.

Fig. 2 Three styles of salt splitting cell for the regeneration of caustic and sulfuric acid from sodium sulfate.

Product and brine concentration

Further concentration of the acid and base streams produced by electrolysis may or may not be required, depending on the requirements of downstream users (e.g. leaching, SX stripping, neutralization). For example, to concentrate a stream from 20 wt.% to 40 wt.% requires the removal of 2.5 kg water per kg of dry-basis acid or base. In the present analysis, the cost of concentrating the products was estimated from the heat of evaporation of water ($2260 \, \text{kJ} \, \text{kg}^{-1}$) and an energy economy of 2.0. This figure can be converted to cost by multiplying by the site's known hot utility cost (e.g. natural gas).

In all salt splitting chemistries, some water is co-transported across the membranes alongside the ions. The amount of water transported is only a fraction of the total water entering the system, however, making it necessary to continuously concentrate the brine in order to maintain the water balance of the system; otherwise a large purge is required. A reverse osmosis system is often suitable for this service, although other techniques (e.g. evaporation) can also be used.
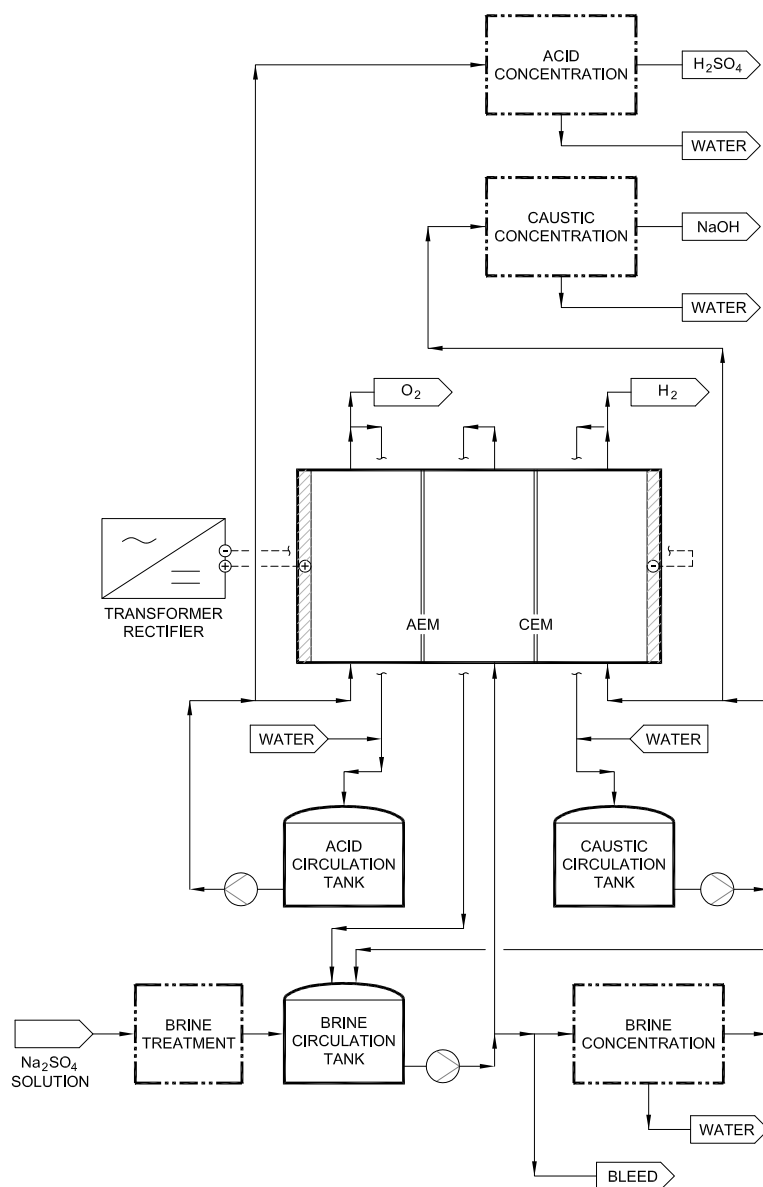
Fig. 3 Schematic of a three compartment sodium sulfate salt splitting plant.

The water thus removed can be added into the acid and caustic circulation loops to maintain their respective water balances. Adding water to the anolyte and catholyte loops, followed by separate product concentration, may appear inefficient and counterintuitive. However, the need to operate the loops within limited concentration ranges to maintain acceptable current efficiency usually makes this necessary.

The overall operating cost of electrolytic salt splitting can be reduced significantly if the downstream users can adapt to using less-concentrated acid and base, or if the membranes are chosen to allow operating with more concentrated anolyte and catholyte.

Maintenance

Isolation points, both electrical and hydraulic, are typically included around banks of cells to allow for modular maintenance. A full-plant shutdown is therefore not needed for most maintenance activities.

Ion exchange membranes degrade over time and must be replaced periodically. A membrane can last as long as four years, or as short as three months, depending on solution composition and how the process is operated. Factors such as unstable operation and calcium buildup can cause premature membrane degradation. Replacement costs can range from several hundred to nearly a thousand dollars per square meter, depending on the material and supplier. Historically, cation exchange membranes are more robust than anion exchange membranes.

The electrodes also need periodic replacement or refurbishment. Oxygen-evolving dimensionally stable anodes (DSAs), which are based on a proprietary formulation of platinum, ruthenium, and iridium oxides on a titanium substrate, are typically sent back to the manufacturer for stripping and recoating. A replacement schedule of 2-5 years is typical, again depending on operating conditions. Cathodes typically require less maintenance and are less costly to replace than anodes.

Maintenance costs can be reduced by following some operational guidelines. The membranes should be protected from excessive cycling, drying, or large swings in salinity, any of which could cause distortion and cracking. Contaminant levels should be monitored closely and kept to a minimum, particularly calcium and magnesium. The maximum recommended current density should not be exceeded. The anode coating should be protected from pH conditions outside of its recommended range.

5 Comparative cost model

The comparative cost of electrolytic salt splitting vs. direct reagent purchase was assessed for sodium sulfate. The results of the analysis are summarized in Figures 4 and 5. Costs are reported in USD per stoichiometric equivalent of 1 tonne of Na_2SO_4: 560 kg of NaOH and 690 kg of H_2SO_4 (both dry basis).

Two different cell styles were assessed: a three-compartment cell producing NaOH on the cathode and H_2SO_4 on the anode, followed by evaporative concentration; and a two-compartment cell producing NaOH on the cathode and a mixed Na_2SO_4-H_2SO_4-$NaHSO_4$ stream on the anode, followed by evaporative concentration of the caustic and a secondary separation step to strengthen the acid and partially reject the salt. Bipolar membrane electrodialysis (BME)
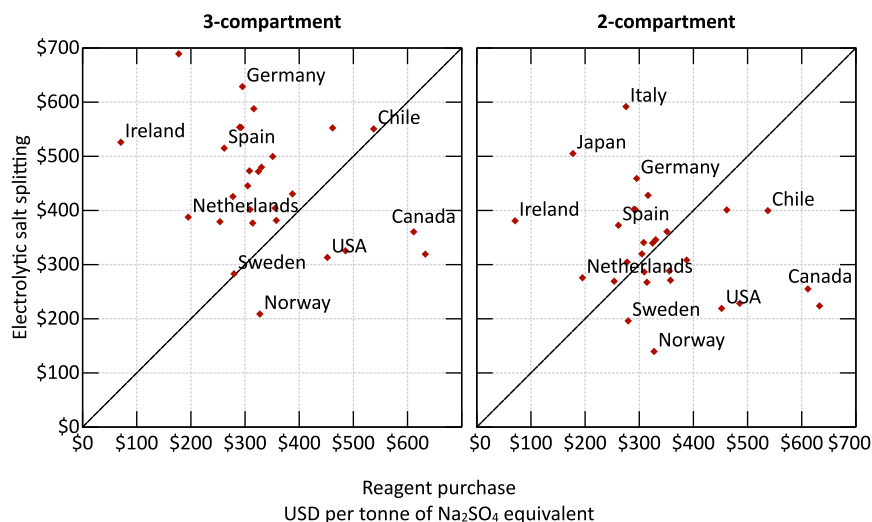

Fig. 4 Operating cost comparison for NaOH and H_2SO_4 production via 2-compartment electrolytic salt splitting vs. market chemical purchase (net of sale revenue of sodium sulfate). Regions above the diagonal line favour purchase, while those below the line favour electrolysis. Costs are reported in USD per stoichiometric equivalent of 1 tonne of Na_2SO_4 (560 kg of NaOH and 690 kg of H_2SO_4, both dry basis)

offers another route that is comparable to three-compartment electrolysis. BME is not assessed in the present work because it is typically associated with production of lower strength reagents than are being considered here.

The parameters used in this cost model are listed in Table 1. Typical values for cell voltage, current efficiency, and product concentrations were assumed, based on NORAM's experience. In reality, these parameters can vary significantly depending on process goals, and are unique to each operation. Electricity prices were estimated using the 2017 national average industrial prices published by the International Energy Agency (International Energy Agency (2017)), which are reproduced in Figure 6. The hot utility cost (e.g. natural gas to generate heat for evaporators) was assumed at 40% of the electricity cost. It is worth noting that electricity prices can vary significantly within a country, and that large users may be able to negotiate a lower rate, so these values should be used with caution. A fixed charge for effluent disposal was also included. Other costs, such as staffing, additional heating/cooling costs, etc., were not included, as these are relatively minor and do not differ significantly between the options.

The cost of procuring an equivalent amount of acid and base at various locations around the world was estimated using world trade data published by the United Nations ComTrade service (United Nations (2018)). This data set provides the annual reported international trade volumes and values for H_2SO_4 (HS code 2807), liquid NaOH (HS code 281512), and Na_2SO_4 (HS code 283311) for most countries in the world. As these chemicals are bulk-traded commodities, the international trade prices can be considered roughly in line with the average prices available domestically in each country, although it is acknowledged that actual prices may vary substantially depending on purity, contract negotiations, etc. The reported values were assumed to be dominated by 96% acid and 50% caustic, which were also the concentrations assumed when calculating the volumes required.
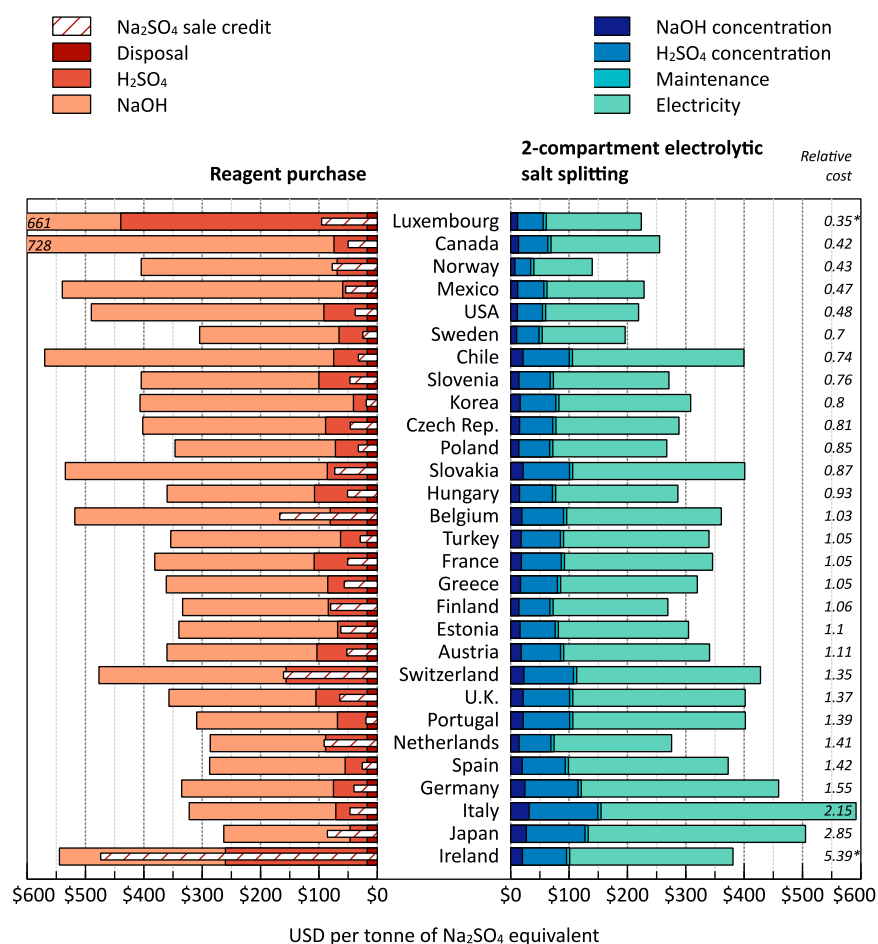

Fig. 5 Breakdown of operating costs for 2-compartment electrolytic salt splitting vs. market chemical purchase. Chemical prices include assumed transportation, handling, and marketing costs. * The relative costs for Ireland and Luxembourg are skewed due to the high sodium sulfate and sulfuric acid prices in those countries, respectively.

Table 1 Assumed operating conditions for the evaluation of a 35 000 t/a NaOH salt splitting plant.

		3-compartment	2-compartment
Cell voltage	V	6.0	4.5
Current density	$A\,m^{-2}$	1500-3000	2500-6000
Current efficiency	%	75	80
AC-DC conv. efficiency	%	93	93
Bus losses	%	5	5
NaOH strength (electrolysis)	wt. %	24	24
NaOH strength (evaporation)	wt. %	50	50
H_2SO_4 strength (electrolysis)	wt. %	9.8	*
H_2SO_4 strength (evaporation)	wt. %	35	*
Electricity	USD/kWh	varies by region	
Chemical prices	USD/t	varies by region	
Transportation	USD/km-t	0.15	
Hot utility	USD/kWh	40% of electricity cost	
Maintenance (overall)	USD/m^2	2500-3500	

*Mixed acid system

The per-country reagent prices were calculated by dividing the total trade value by total trade volume (imports + exports), and are summarized in Figures 7 to 9, with select countries labeled. A country was considered import- or export-dominant if more than 90% of its trade is in one direction. A 10% premium was added to the NaOH and H_2SO_4 prices to reflect supply chain costs, and a transport charge of $0.15\,USD/t - km$ was added, assuming 100 km distance to the nearest port or distribution facility. A credit was also applied for the sale of Na_2SO_4, with a 50 % penalty applied to reflect the potential difficulty of marketing the product. This is optimistic, since the realizable resale value of sodium sulfate would be considered negligible at many sites, or not worth the investment. Finally, a disposal cost of $2.60\,USD/m^3$ was assumed for the barren solution.

6 Capital cost and rate of return

The capital costs of the two salt splitting concepts described above were estimated based on factored equipment costs and scaled data from prior NORAM projects. The estimates include the cell house, piping, transformer-rectifier, circulation tanks and pumps, and evaporators. Excluded are any site infrastructure costs, such as the construction of an electrical substation, civil works, building, etc.

The estimated cost of a 35 000 t/a NaOH salt splitting plant using all the assumptions listed in Table 1 is 57 M USD for a three-compartment cell house or 34 M USD for a two-compartment cell house (2017 dollars). The significantly lower capital cost of a two-compartment cell house is due mainly to the higher current density, which allows for the same production to be achieved in a smaller facility, as well as lower maintenance costs.

The internal rate of return (IRR) for a three-compartment cell house (vs. reagent purchase) is usually negative, but can exceed 20% in the most favourable cases with the right combination of low electricity prices and high chemical prices. The IRR is higher for a two-compartment cell house, owing to the significantly lower capital cost and the lower operating costs. The IRR could be improved in both cases by reducing or eliminating the need for product concentration (evaporators/crystallizers).

7 Analysis and conclusions

This study shows that, in most cases, and under today's market conditions, salt splitting in a three-compartment cell with a subsequent concentration step often costs more than simply purchasing the reagents at market prices. Significant savings can be realized by using a two-compartment cell, but with the trade-off that it produces an acid-salt mixture that may require further purification. The case is strongest in places with inexpensive power, high disposal costs, and high reagent and transport costs.
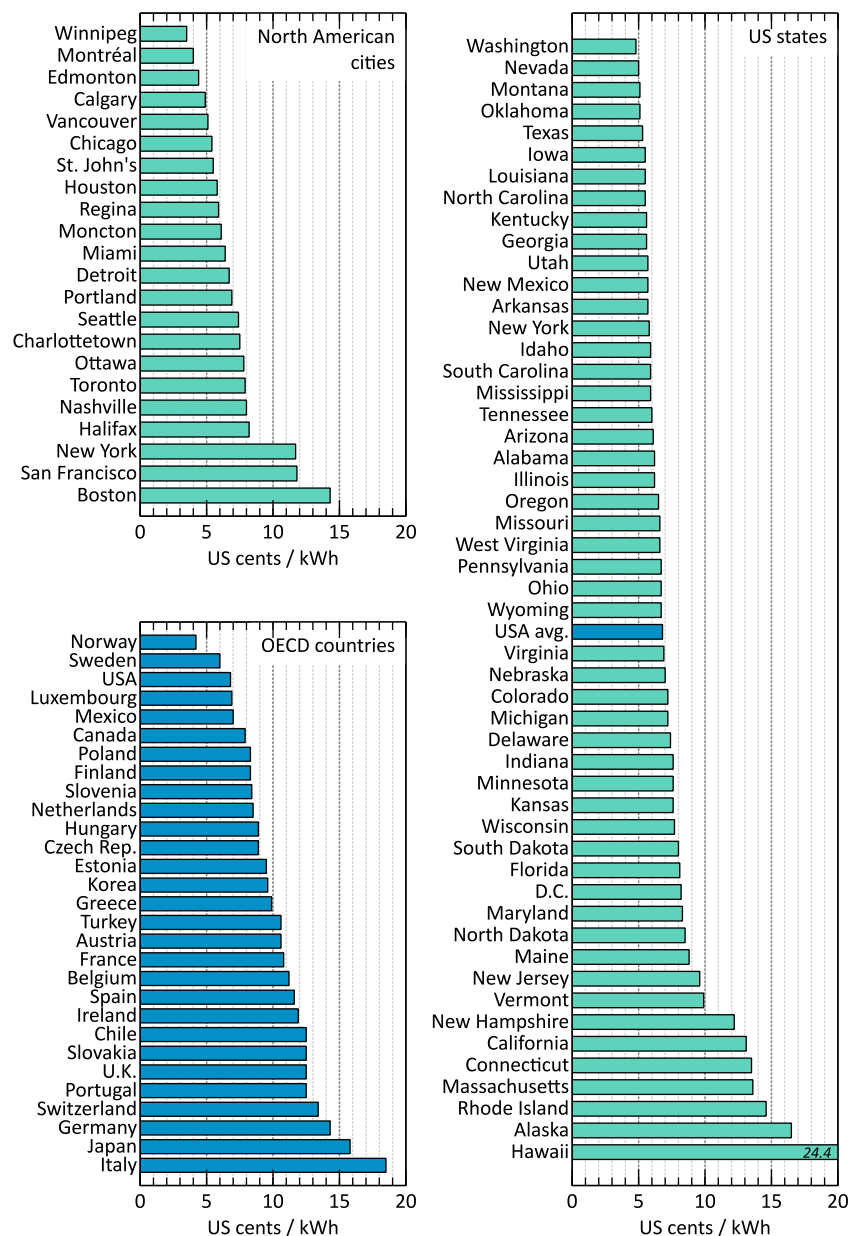
Fig. 6 Published industrial electricity prices, latest available. North American city data from Hydro Quebec (2017), 10,000 kW large user, 1.26 CAD = 1 USD currency conversion. US state data from U.S. Energy Information Administration (2018), industrial user. OECD data from, International Energy Agency (2017), industrial user.

Given that the economic case for electrolytic salt splitting is marginal in most regions, why should it be considered at all? The most compelling case involves two related issues that are increasingly relevant in hydrometallurgy: salt disposal and water use. The total salinity of plant effluent is facing increasing scrutiny in many jurisdictions, both in response to shifting public perception of environmental issues, and in response to an increasing body of research that suggests that some ions such as sulfate, though not toxic themselves, can harm the environment in other ways (van Dam et al (2014)). By applying salt splitting, a large portion of the salt is recovered, reducing the effluent loading. Similarly, restrictions on water use may incentivize a process that enables the internal recycling of water. Electrolytic salt splitting recovers water alongside acid and base. An operation's environmental credentials can also be bolstered if a low-carbon source of electricity is available, such as hydroelectric. These elements contribute to an operation's social licence to operate.

Electrolytic salt splitting of sodium sulfate can be implemented today, using existing and proven technologies. Doing so can dramatically reduce net reagent consumption, water use, and waste. However, the relatively low costs of sulfuric acid and caustic today may in many cases make the operating and capital costs difficult to justify on economic grounds alone, except under certain circumstances. A more compelling case may be made for other systems, such as chloride-based chemistries, or as an enabling technology for a novel process. Nevertheless, the case for electrolytic salt splitting of sodium sulfate continues to strengthen as the economic and social climate evolves, and in particular as sodium hydroxide prices rise, making it something worth considering at any operation with a sodium sulfate waste stream.

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<u>Correction (2018-08-22)</u>
The version of this article published in the Proceedings of the Extraction 2018 conference (Ottawa) contains an error in Figure 3. The figure shown here has been corrected.
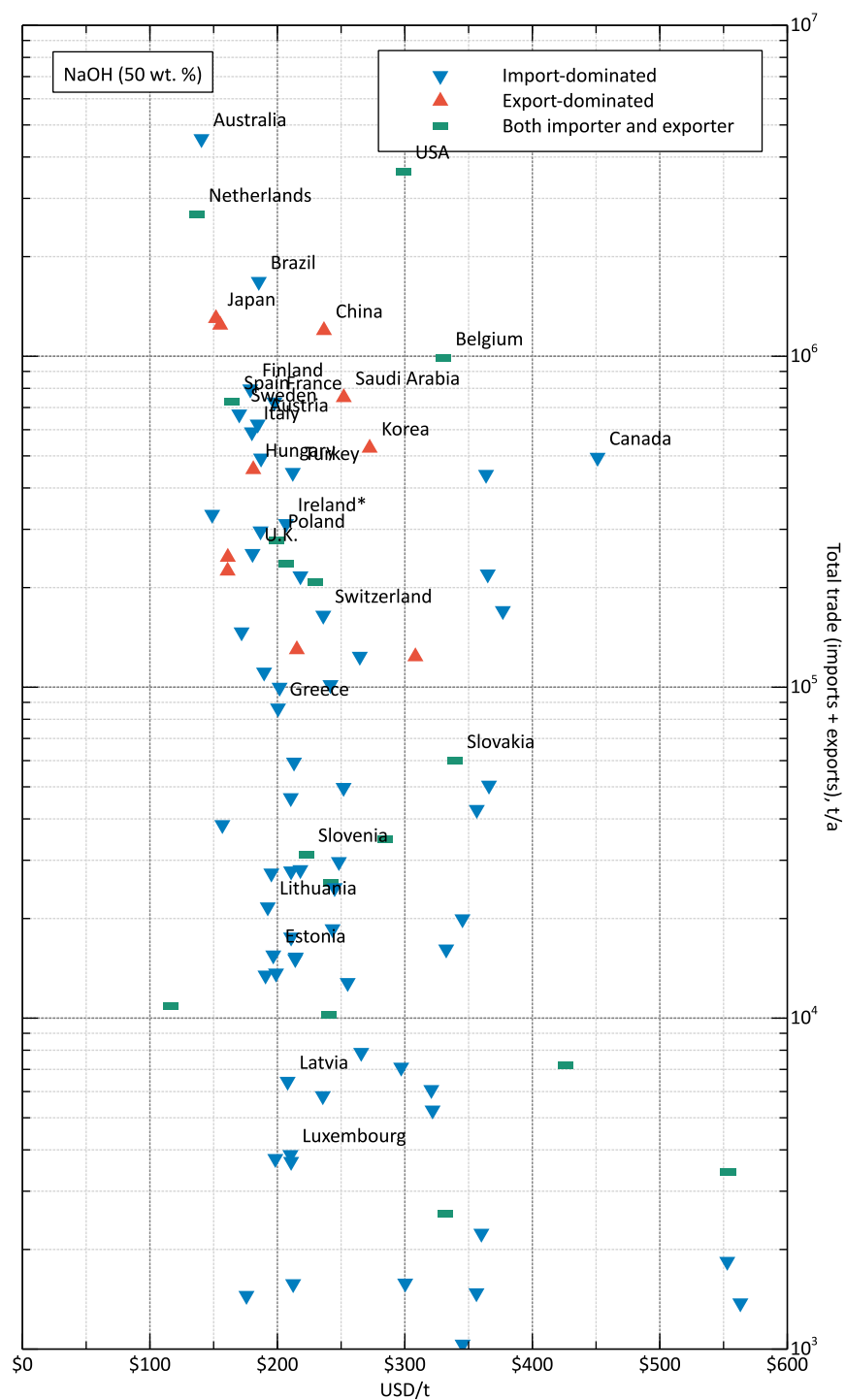
Fig. 7 Sodium hydroxide (50 wt. %) average international trade price, by country. From UN Comtrade 2016 data, HS code 281512: sodium hydroxide in aqueous solution. United Nations (2018)
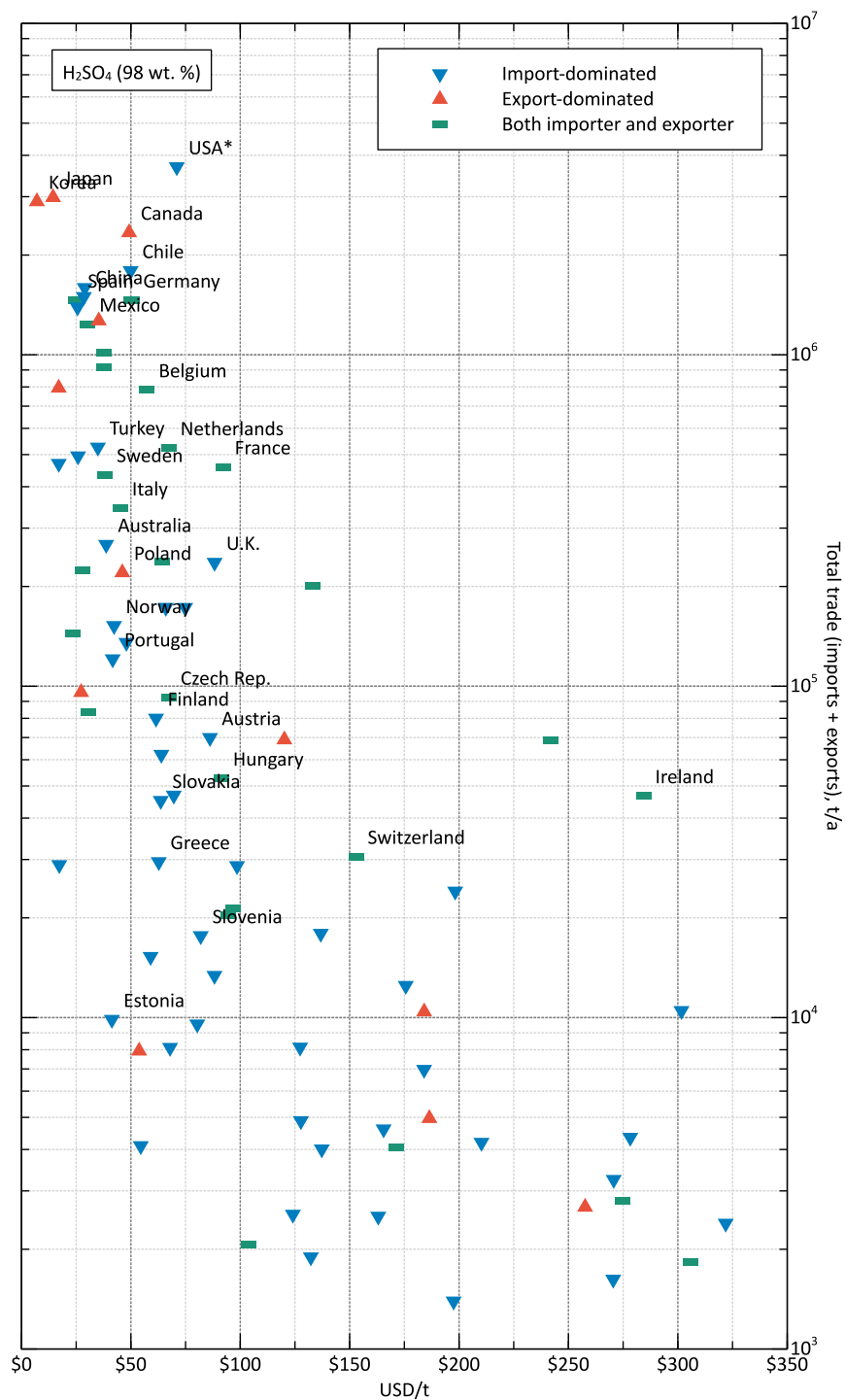
Fig. 8 Sulfuric acid average international trade price, by country. From UN Comtrade 2016 data, HS code 2807: sulphuric acid. United Nations (2018). * USA data from 2015.
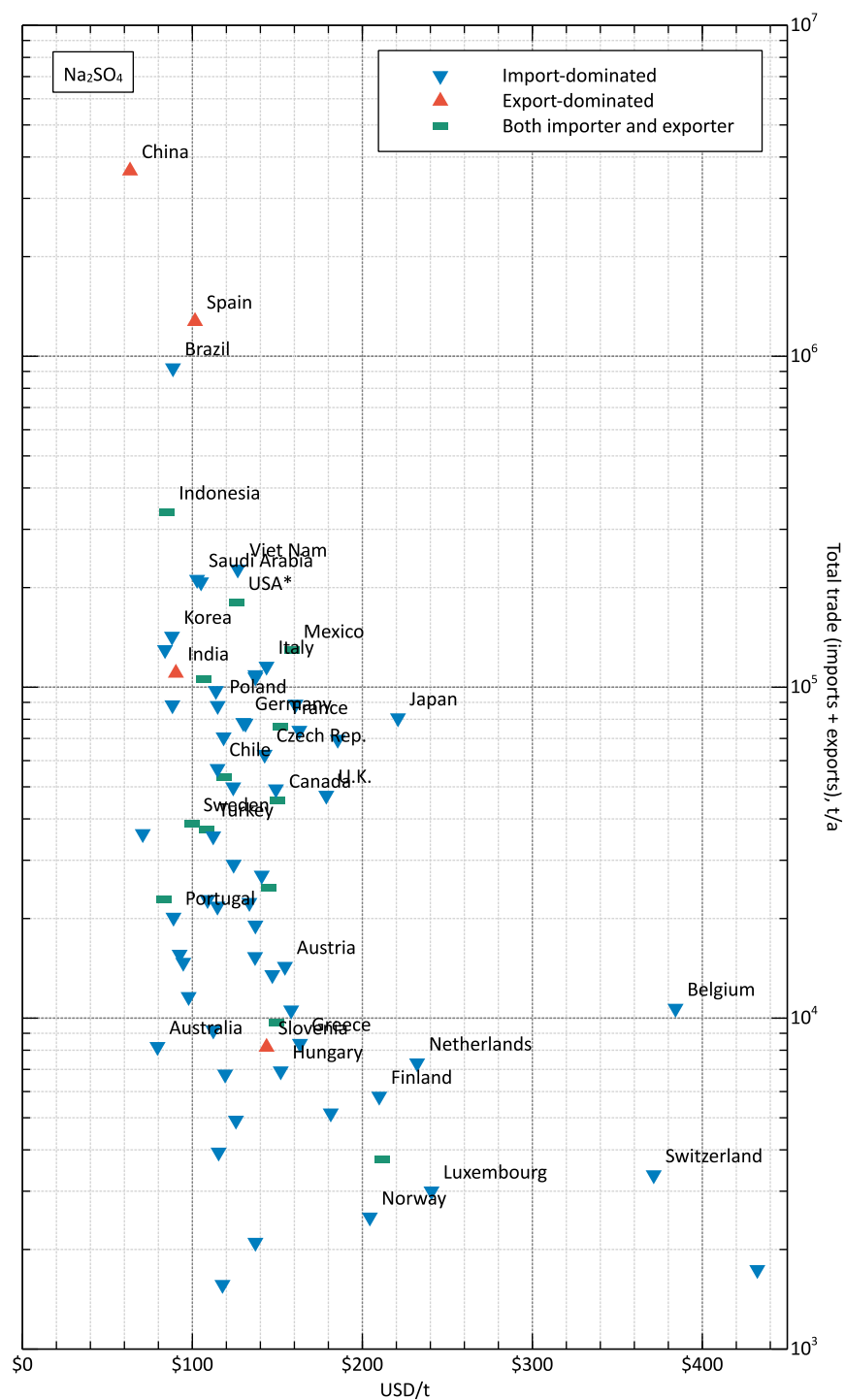
Fig. 9 Sodium sulfate average international trade price, by country. From UN Comtrade 2016 data, HS code 283311: disodium sulphate. United Nations (2018). *USA data from 2015.