The missing link in circular hydrometallurgy: efficient splitting of salts in acids and bases

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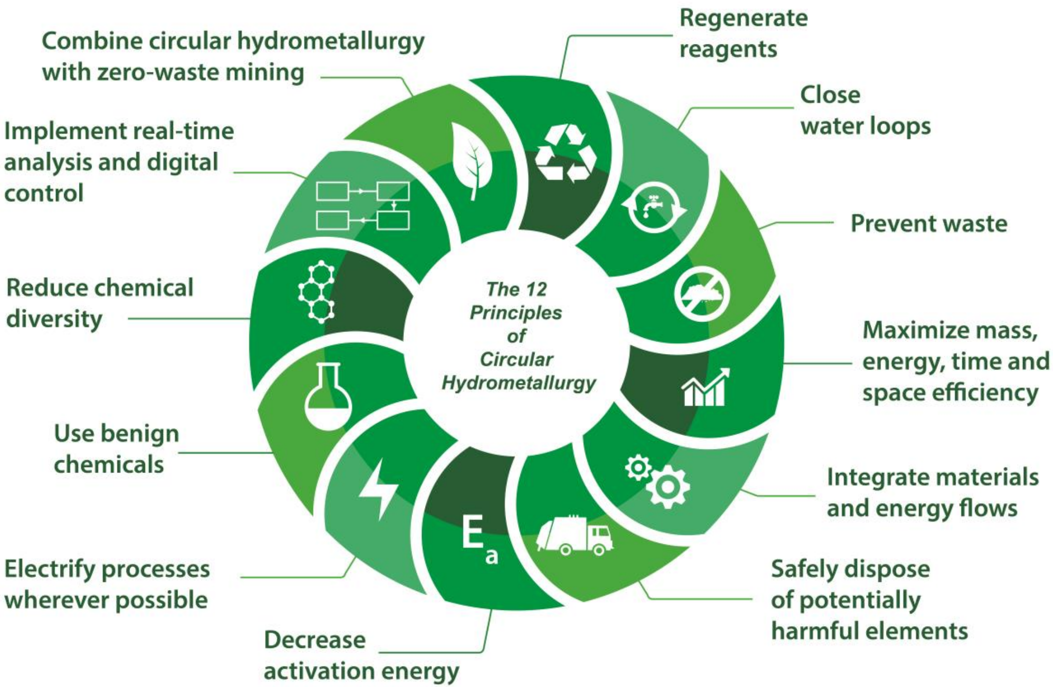
SOLVOMET
CIRCULAR HYDROMETALLURGY

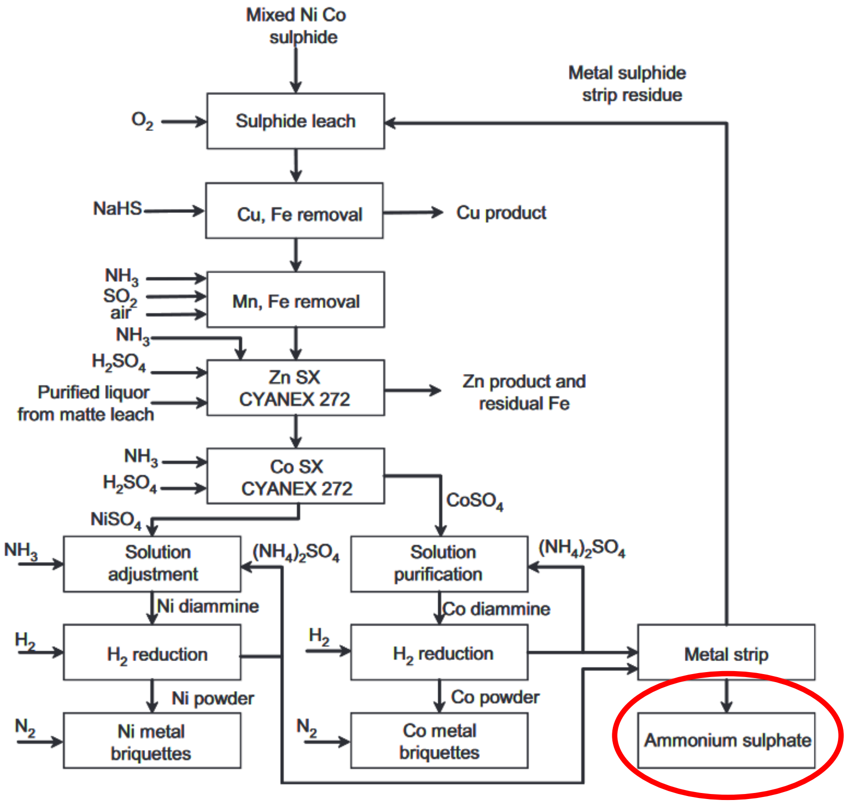
KU LEUVEN SIM2
Sustainable Inorganic Materials Management



Many hydrometallurgical processes produce salt waste streams

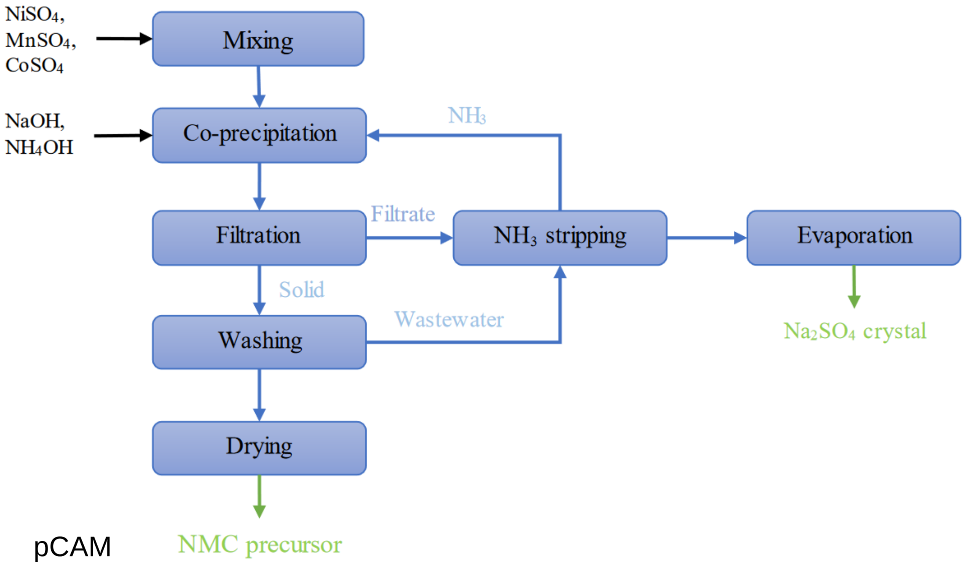
- Dissolution of carbonate gangue minerals during acid leaching
- Oxidative ammoniacal leaching of sulphidic ores or concentrates
- Neutralisation of excess acid after leaching to increase pH (to precipitate Fe^{3+} and Al^{3+})
- Co/Ni refining by solvent extraction with acidic extractants
- Refining of rare-earth elements (REEs)
- Li_2CO_3 formation from LiCl or Li_2SO_4 by reaction with Na_2CO_3
- Production of precursors of cathode-active materials (pCAM)
- ….

Oxidative ammoniacal leaching of sulphidic ores (Sherritt Gordon process) generates $(NH_4)_2SO_4$



Source: K.C. Sole et al. *Hydrometallurgy* **78** (2005) 52–78

Vast amounts of Na_2SO_4 are produced during synthesis of pCAM (NMC precursor) by coprecipitation



≈ 1.5 tonne Na_2SO_4 / 1 tonne pCAM

Source: https://greet.es.anl.gov/publication-update_bom_cm

Source: https://cen.acs.org/energy/battery-industrys-sodium-sulfate-waste/102/i21

Na_2SO_4 is a problematic waste stream because it cannot be landfilled and market cannot absorb the amounts produced

Water soluble

Reduced to H_2S by sulphate-reducing bacteria

Discharge limits for sulphates

Declining solid detergents market

Limited potential for Na_2SO_4 to K_2SO_4 conversion by KCl

Reliable supply chain already existing; no need for extra suppliers

Natural Na_2SO_4 preferred over synthetic product

Na_2SO_4 waste is a threat for the battery industry

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CHEMICAL & ENGINEERING NEWS

POLLUTION

BASF battery project delayed because of environmental concerns

Other firms building battery materials plants in the US and Europe could face similar permitting hurdles

by *Matt Blois*

February 29, 2024 | A version of this story appeared in **Volume 102, Issue 7**

What to do with the battery industry's sodium sulfate waste?

The by-product is raising environmental concerns as companies race to build new plants

by *Matt Blois*

July 9, 2024 | A version of this story appeared in **Volume 102, Issue 21**

Salt splitting is the conversion of a salt in its corresponding acid and base. It is the reverse reaction of neutralisation

Neutralisation

Acid + Base → Salt + Water

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Salt splitting

Salt + Water → Acid + Base

$Na_2SO_4 + 2H_2O \rightarrow H_2SO_4 + 2NaOH$

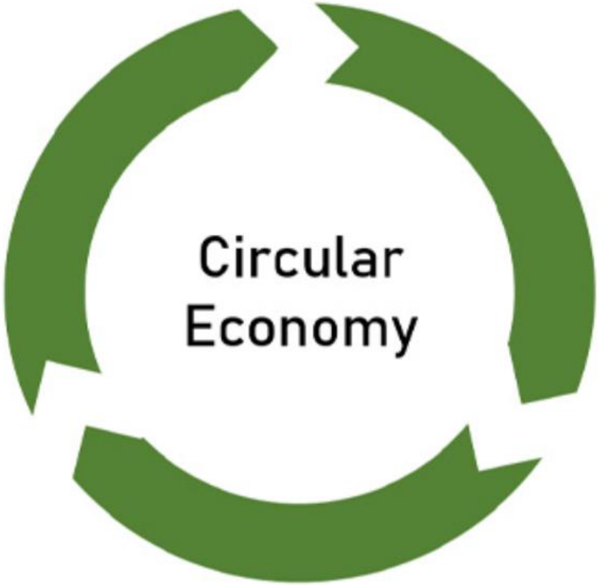
Salt splitting offers many advantages

Less consumption of reagents

Lowering production costs

Independent of commodity chemicals supply

Price stability and supply security



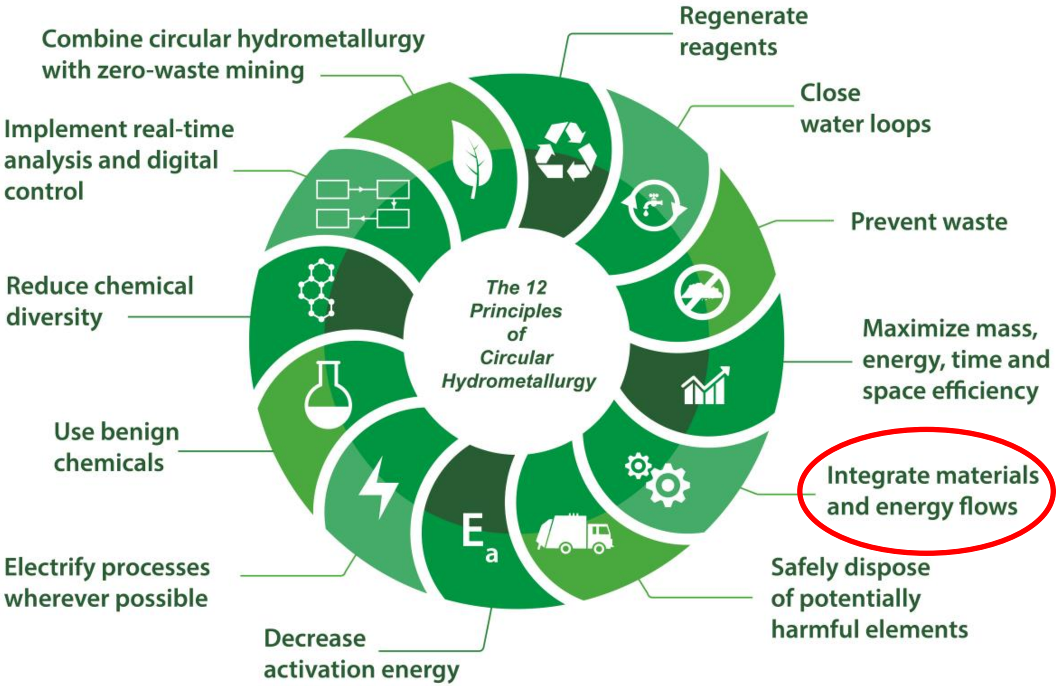
Less transport of chemical reagents to production site

Smaller CO_2 footprint

Minimising environmental impact

Easier to get environmental permits

On-site salt splitting is example of principle “Integrate Materials and Energy Flows” in circular hydrometallurgy



Less transport of chemicals

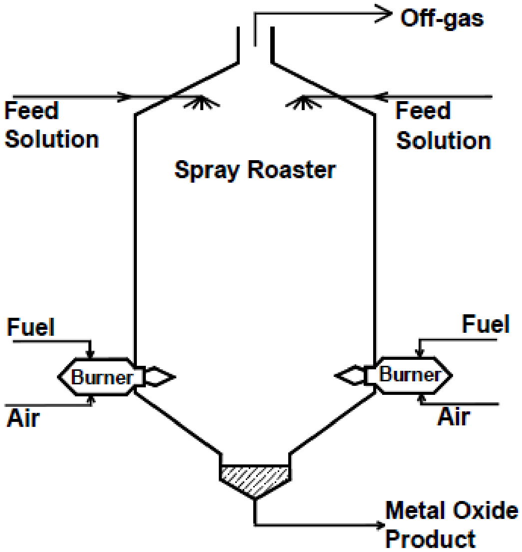
Less losses of waste heat (= higher energy efficiency)

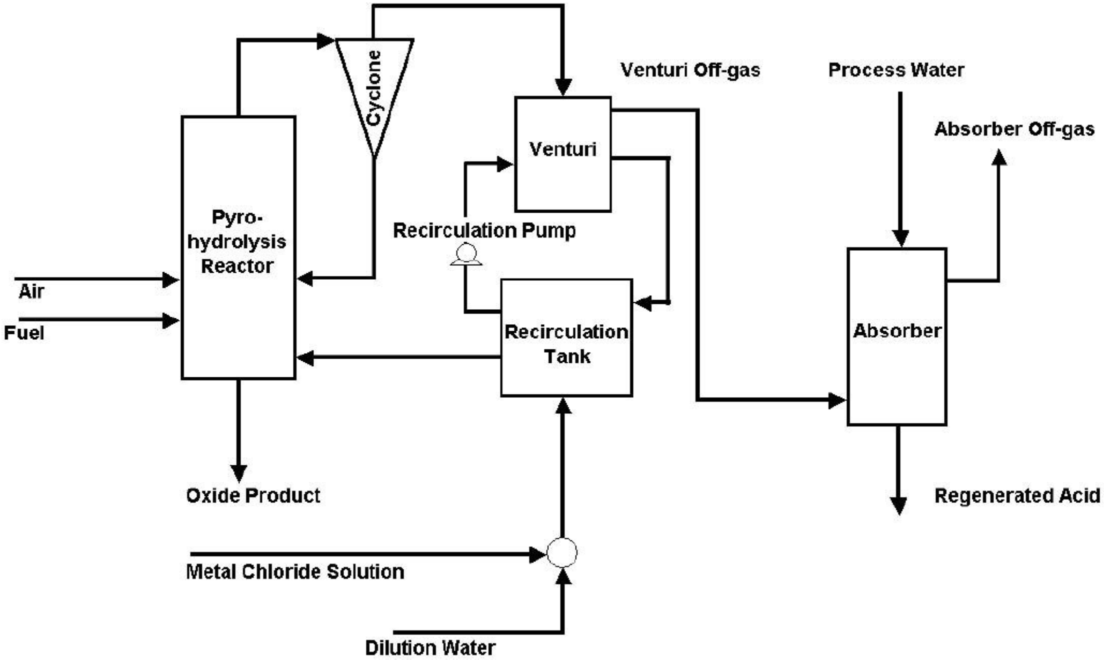
Less impurity constraints

Less water evaporation needed (lower acid concentrations acceptable)

Although more expensive, HCl and HNO_3 are easier to regenerate than H_2SO_4

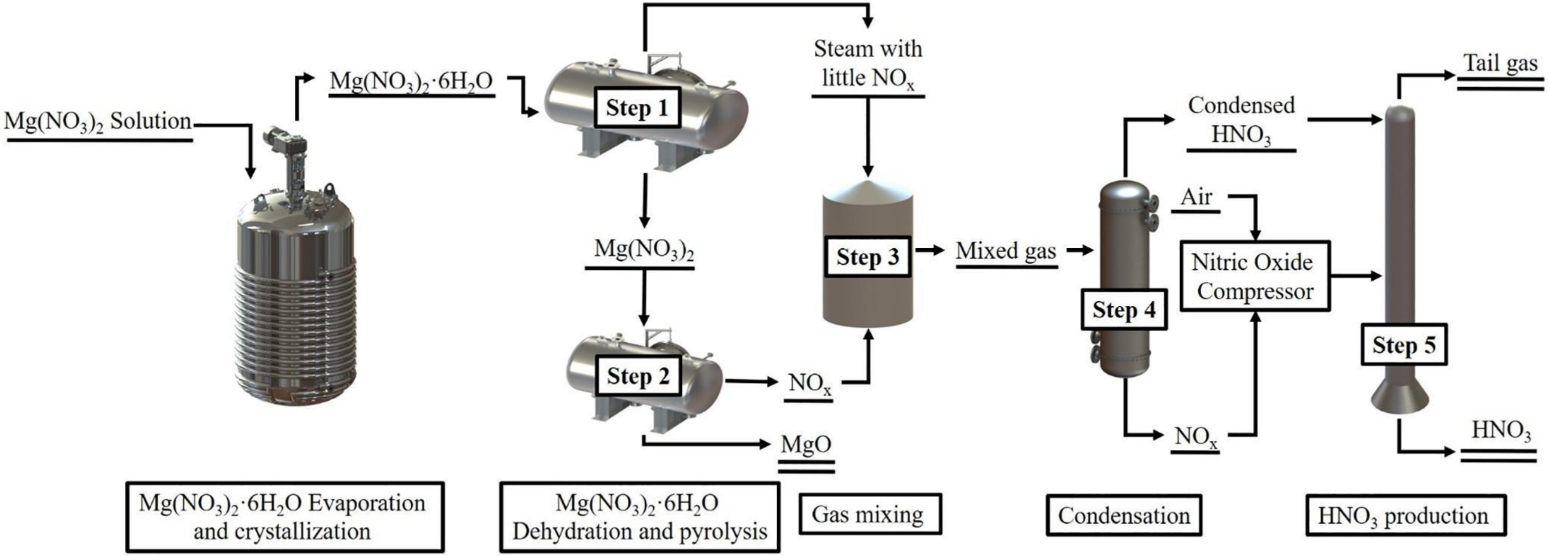
Pyrohydrolysis is a well-established method for converting metal chlorides into HCl and (basic) oxides, but is energy-intensive





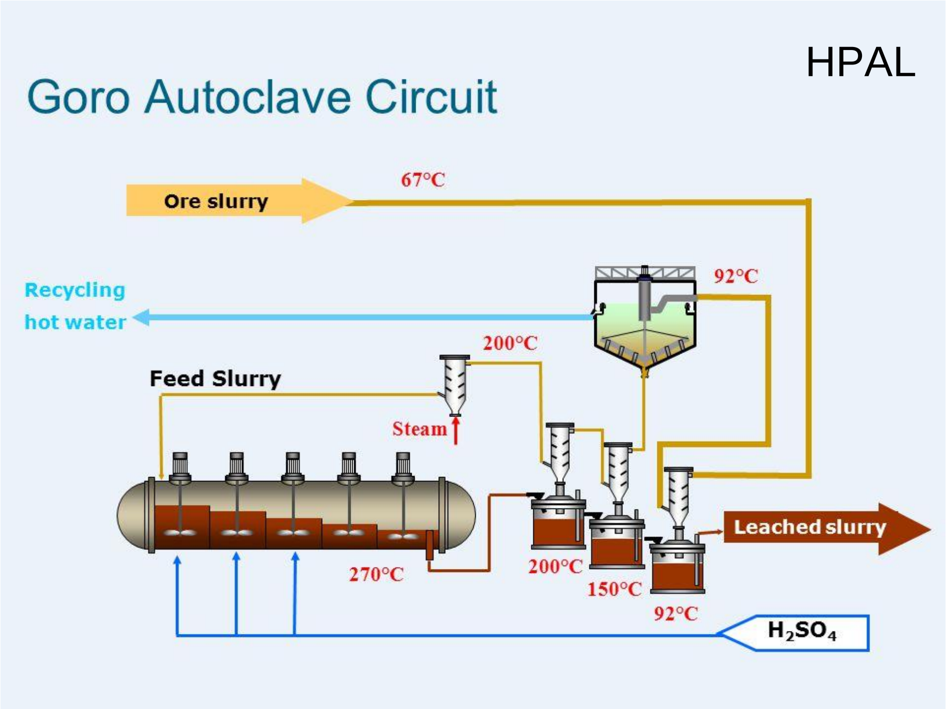
Source: Adham and Li, Chloride Metallurgy 2002

Pyrolysis of nitrates of alkaline earth metals (Mg, Ca) regenerates HNO_3 and basic oxides (MgO, CaO)

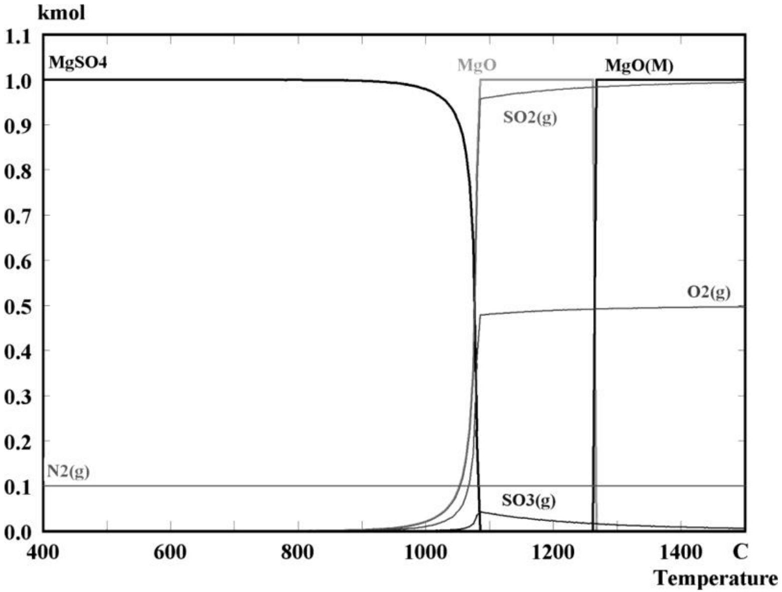


Source: D. Zhao et al., *Chem. Eng. J.* **433** (2022) 133804

H_2SO_4 is the cheapest and most often used acid in hydrometallurgy, but it is not so easy to regenerate thermally



Source: VALE INCO



Source: M.N. Scheidema, P. Taskinen, *Ind. Eng. Chem. Res.* **50** (2011) 9550

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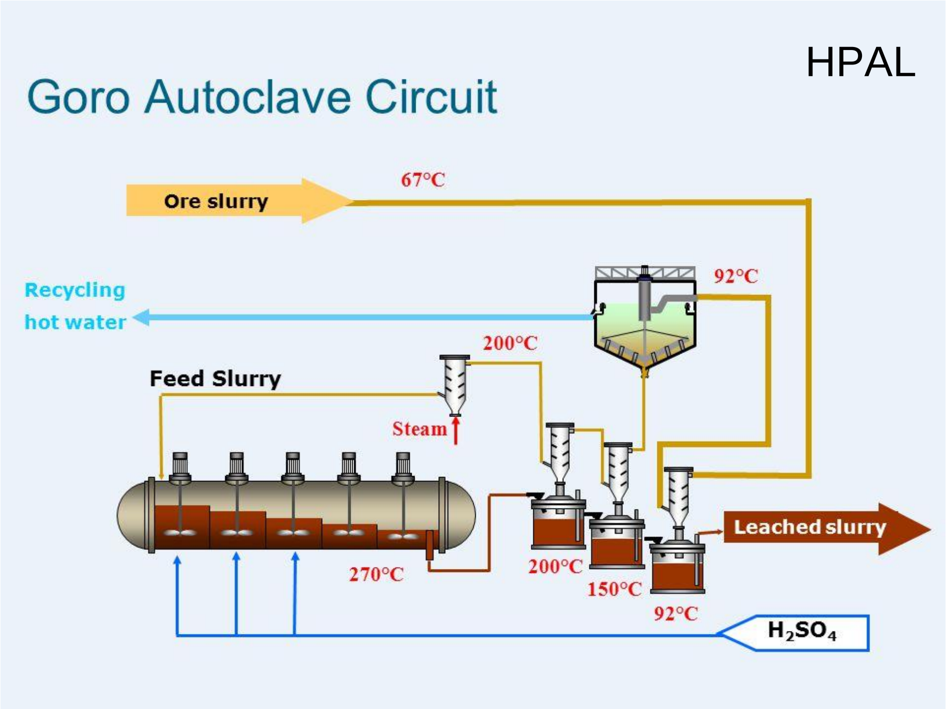

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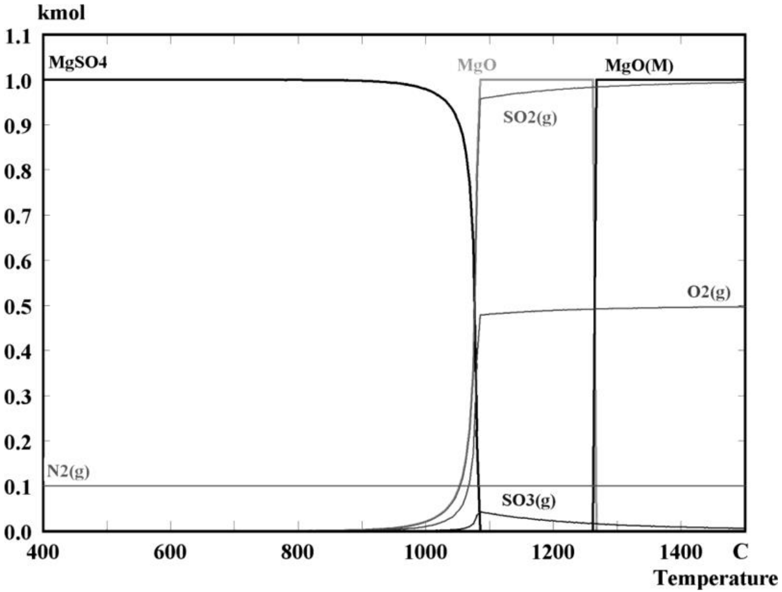
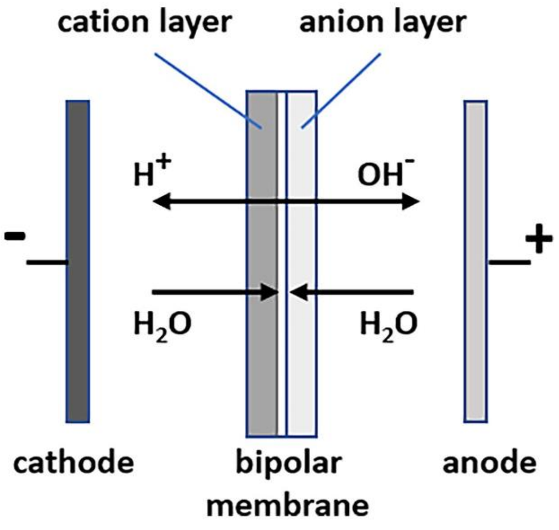
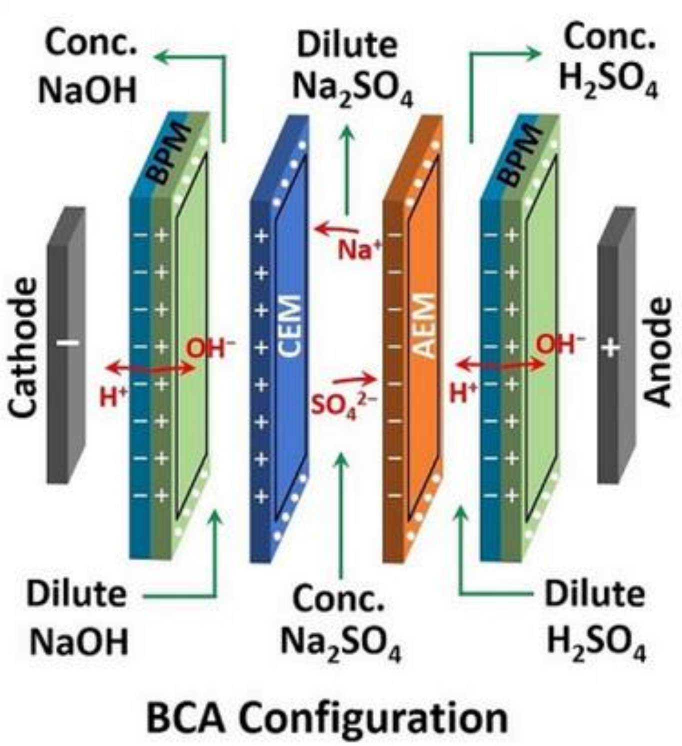


Source: M.N. Scheidema, P. Taskinen, *Ind. Eng. Chem. Res.* **50** (2011) 9550

Bipolar Membrane Electrodialysis (EDBM): bipolar membranes allow for dissociation of water in the presence of electrical field





Source: I. Miesiac, B. Rukowicz, *Electrocatalysis* **13** (2022) 101

Source: Kuldeep et al. *Membranes* **11** (2021), 718

BMED is technologically feasible on industrial scale, but suffers from shortcomings

High CAPEX

High power consumption

Low current densities

Low throughput

Membrane fouling

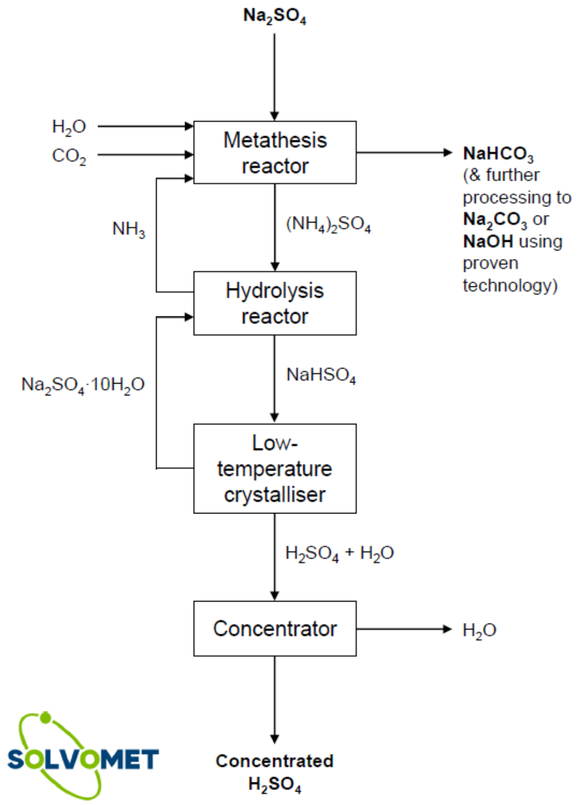
Source: https://ion-exchangemembrane.com

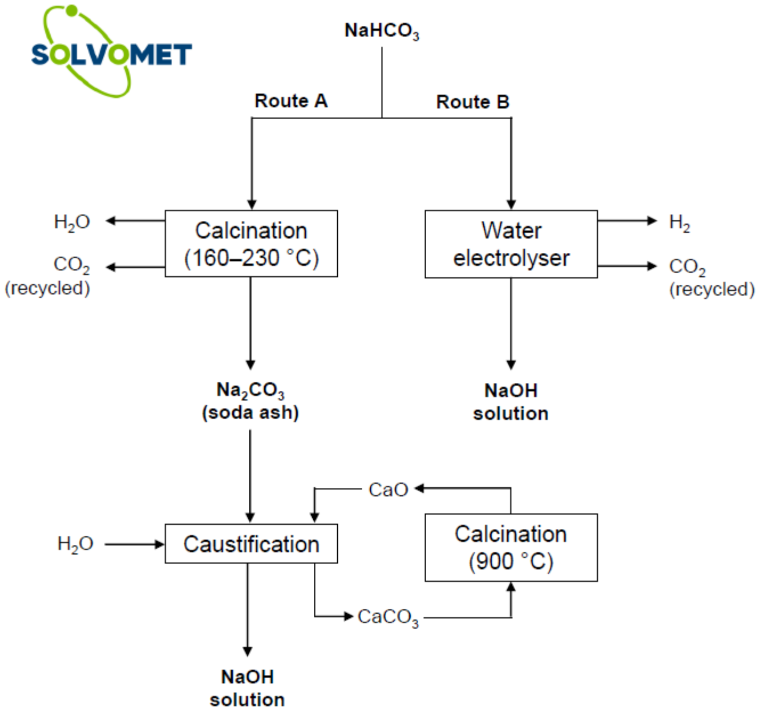
Low feed concentration (< 150 g/L Na_2SO_4)

Quality NaOH and H_2SO_4 is often too low

Cheap electricity must be available to make process economically feasible

Advanced conversion of sulphate salts in circular hydrometallurgy (ADONIS process)





Key component in acid generation is ammonium sulphate, since ammonium ion can be hydrolysed to ammonia gas

- **Metathesis reaction (modified Solvay process)**

$$Na_2SO_4 + 2NH_3 + 2CO_2 + 2H_2O \leftrightarrows 2NaHCO_3 + \mathbf{(NH_4)_2SO_4}$$

- **Hydrolysis reaction (110–120 °C)**

$$\mathbf{(NH_4)_2SO_4} + Na_2SO_4 \leftrightarrows 2NaHSO_4 + 2NH_3\uparrow \quad \text{(in water)}$$

- **Low-temperature crystallisation (< 0 °C)**

$$2NaHSO_4 + xH_2O \leftrightarrows Na_2SO_4{\cdot}10H_2O\downarrow + H_2SO_4 + (x\text{–}10)H_2O$$

Solubility of $Na_2SO_4 \cdot 10H_2O$ rapidly decreases when temperature falls and presence of H_2SO_4 suppresses solubility even further

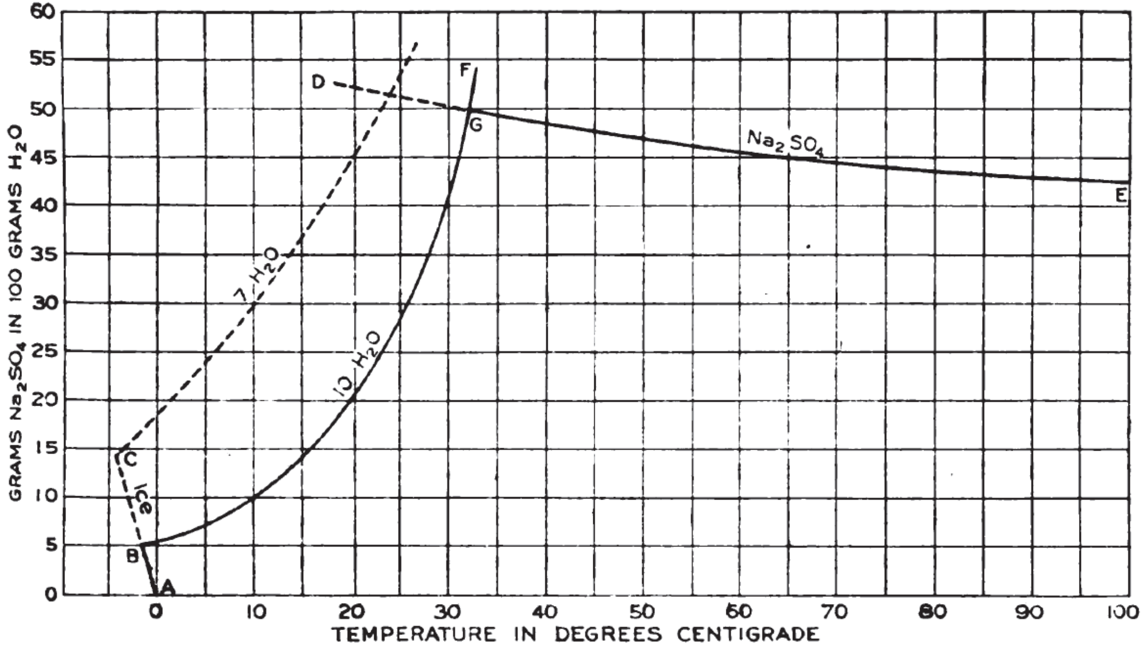


FIGURE 3.—Solubility of sodium sulphate in water.

From 10 tons of nitre cake there are obtained 15 tons of Glauber's salt and 11 tons of an acid solution containing 26.8% H_2SO_4 and 2.8% Na_2SO_4. By further cooling it is possible to reduce further the proportion of sodium sulphate in the final liquor.

ADONIS process is based on 19th century and early 20th century inorganic chemistry

1874

Ueber die Dissociation der Ammoniumsalze in wässeriger Lösung.

Von

Dr. H. C. Dibbits.*)

Die Anleitung zu den folgenden Versuchen, deren Resultate ich hier auszugsweise mittheile, war die von mir gemachte Beobachtung, dass bei der quantitativen Bestimmung des Ammoniaks als Chlorammonium jedesmal, wenn man das auf dem Wasserbade eingedampfte Salz, nach der Vorschrift H. Rose's, zur Vertreibung der letzten Spuren freier Salzsäure, mit Wasser befeuchtet und wieder bei 100 ⁰ trocknet,

1876

Ueber die Zersetzung einiger Ammoniumsalze in wässeriger Lösung durch Kalium- und Natriumsalze.

Von

Dr. H. C. Dibbits.*)

Nachdem ich in einer früheren Abhandlung**) gezeigt habe, dass verschiedene Ammoniumsalze, beim Kochen ihrer wässerigen Lösung, eine bestimmte Quantität Ammoniak verlieren, welche, ausser von der Quantität und der Concentration der Lösung und von der Quantität des verdampften Wassers, von der Natur des Salzes abhängt, wandte ich mich zur Bestimmung des entweichenden Ammoniaks aus Lösungen, welche,

1906

Hydrolyse von Ammoniumsalzen;

von

Alex. Naumann und **Adolf Rücker.**

(Hierzu 4 Tafeln.)

(Aus dem chemischen Universitätslaboratorium zu Gießen.)

I. Versuchsverfahren.

Nach dem vorbeschriebenen Versuchsverfahren ¹) wurde die Hydrolyse einiger Ammoniumsalze beim Siedepunkt ihrer wäßrigen Lösungen bestimmt.

1918

UNITED STATES PATENT OFFICE.

EDWARD HART, OF EASTON, PENNSYLVANIA.

METHOD OF UTILIZING NITER CAKE.

1,258,895. Specification of Letters Patent. Patented Mar. 12, 1918.

No Drawing. Application filed May 24, 1917. Serial No. 170,607.

To all whom it may concern:

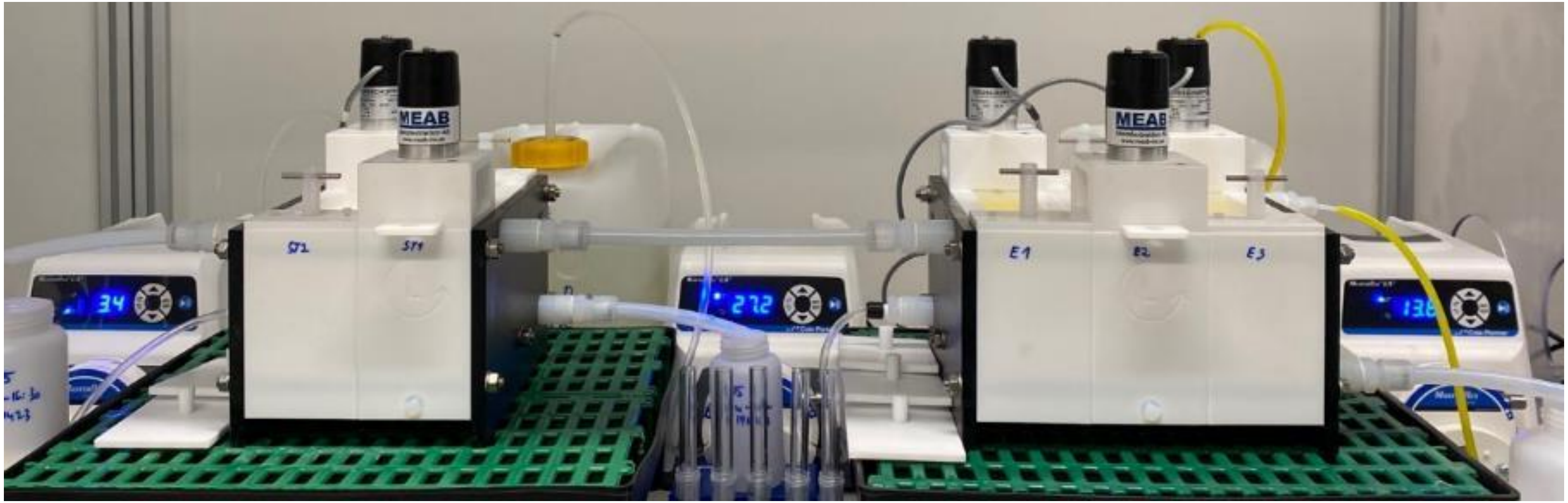
Be it known that I, EDWARD HART, a citizen of the United States, residing at Easton, in the county of Northampton and State of Pennsylvania, have invented certain new and useful Improvements in Methods of Utilizing Niter Cake, of which the following is a full, clear, and exact description.

This invention relates to the utilization of

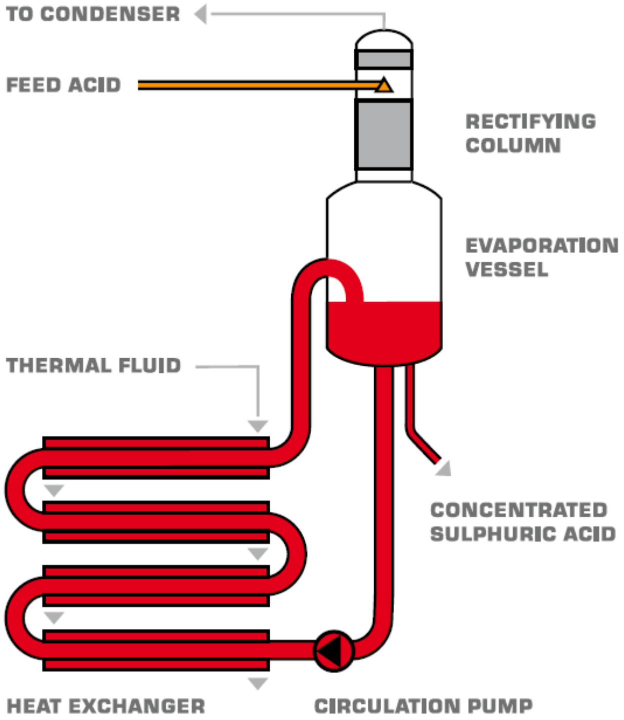
nearly all the sulfuric acid is concentrated by the usual method of concentrating sulfuric acid to remove all or nearly all the water, and is run still warm into the nitric acid still for the treatment of a fresh charge of nitrate.

The method of crystallizing the sulfate is an important feature. In prior processes the foregoing is effected by means of ordinary

H_2SO_4 can be concentrated and separated from Na_2SO_4 by SX with tris(2-ethylhexyl) amine (TEHA) and 1-octanol



Final concentration of H_2SO_4 to 96% can be done by state-of-the-art technology



Source: Bertrams

Different bases can be prepared from $NaHCO_3$ with regeneration of CO_2 reagent

- **Soda ash (Na_2CO_3) by calcination of $NaHCO_3$**

  $2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$

- **Sodium hydroxide (NaOH) by caustification of Na_2CO_3**

  $Na_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2NaOH$

  $CaCO_3 \rightarrow CaO + CO_2$

- **Electrochemical generation of NaOH from $NaHCO_3$ (water electrolyser)**

  Cathode: $2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$

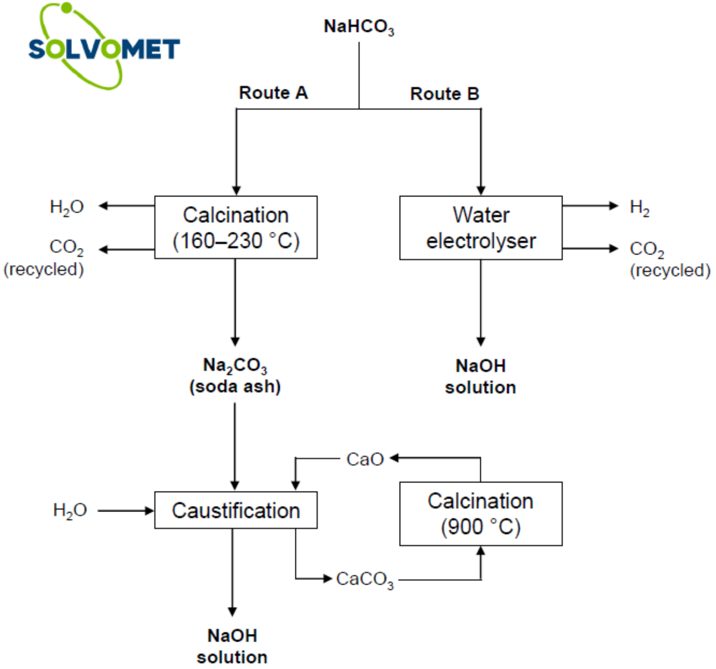
  Anode: $H_2O \rightarrow 1/2\ O_{2(g)} + 2\ H^+_{(aq)} + 2e^-$

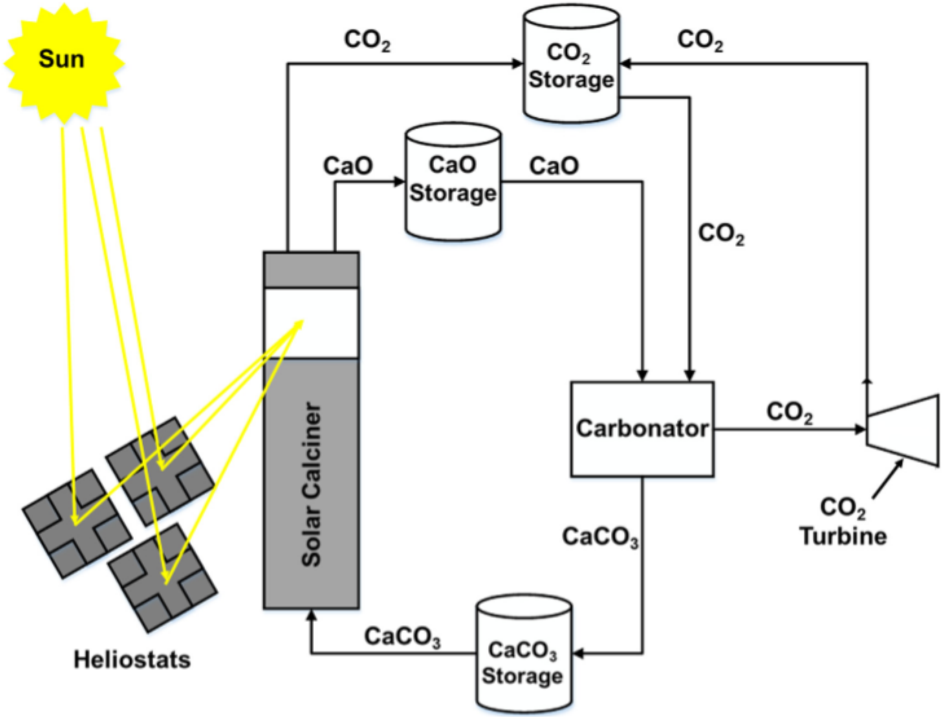
  $H^+ + HCO_3^- \rightarrow H_2CO_3$

  $H_2CO_3 \rightarrow H_2O + CO_2$

Sustainability can be improved by solar calcination of $CaCO_3$ (calcium looping)

SOLVOMET





Source: A.A. Khosa and C.Y. Zhao, *Solar Energy* **188** (2019) 619-630

The ADONIS approach can be extended to acids other than H_2SO_4

- **Hydrochloric acid**

$$2NaCl + H_2SO_4 + xH_2O \leftrightarrows Na_2SO_4 \cdot 10H_2O\downarrow + 2HCl + (x-10)H_2O$$

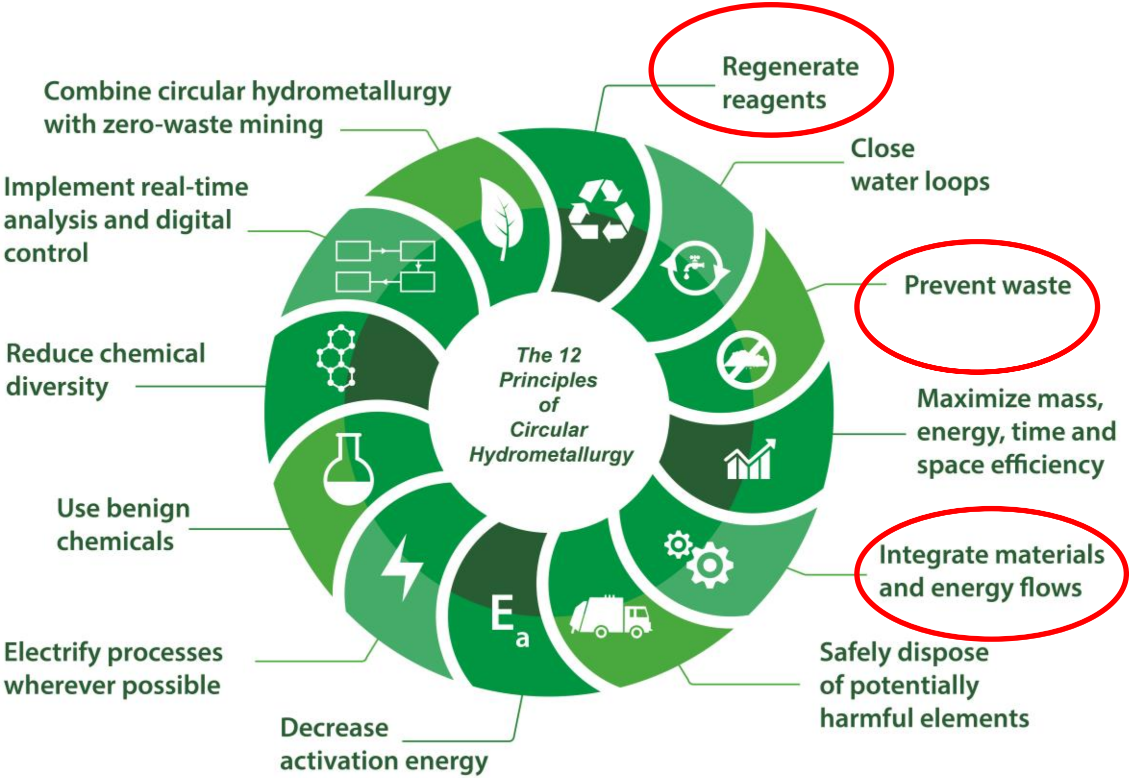
- **Nitric acid**

$$2NaNO_3 + H_2SO_4 + xH_2O \leftrightarrows Na_2SO_4 \cdot 10H_2O\downarrow + 2HNO_3 + (x-10)H_2O$$

- **Methanesulphonic acid (MSA)**

$$2CH_3SO_3Na + H_2SO_4 + xH_2O \leftrightarrows Na_2SO_4 \cdot 10H_2O\downarrow + 2CH_3SO_3H + (x-10)H_2O$$

In conclusion, salt splitting is essential step in circular hydrometallurgy



Thank you for your attention!

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