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The Twelve Principles of Circular Hydrometallurgy

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Table S1. The 12 Principles of Green Chemistry [1]

1. **Prevention**. It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom Economy**. Synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Syntheses**. Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Design Safer Chemicals**. Chemical products should be designed to preserve efficacy of function while reducing toxicity.
5. **Safer Solvents and Auxiliaries**. The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.
6. **Design for Energy Efficiency**. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstock**. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives**. Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis**. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation**. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-time Analysis for Pollution Prevention**. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention**. Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Table S2. The 12 Principles of Green Engineering [2]

1. Inherent rather than circumstantial
2. Prevention instead of treatment
3. Design for separation
4. Maximize mass, energy, space, and time efficiency
5. Output-pulled versus input-pushed
6. Conserve complexity
7. Durability rather than immortality
8. Meet need, minimize excess
9. Minimize material diversity
10. Integrate local material and energy flows
11. Design for commercial “afterlife”
12. Renewable rather than depleting

Table S3. The Sandestin Declaration: 9 Principles of Green Engineering [3]

1. Engineer processes and products holistically, use systems analysis, and integrate environmental impact assessment tools
2. Conserve and improve natural ecosystems while protecting human health and well-being
3. Use life-cycle thinking in all engineering activities
4. Ensure that all material and energy inputs and outputs are as inherently safe and benign as possible
5. Minimize depletion of natural resources
6. Strive to prevent waste
7. Develop and apply engineering solutions, while being cognizant of local geography, aspirations, and cultures
8. Create engineering solutions beyond current or dominant technologies; improve, innovate, and invent (technologies) to achieve sustainability
9. Actively engage communities and stakeholders in development of engineering solutions

Examples of (near) circular hydrometallurgical flowsheets

Now that the Twelve Principles of circular hydrometallurgy have been introduced, we can assess how circular today's previously developed and/or present flowsheets are. In this Section we review four different hydrometallurgical flowsheets that already incorporate a significant number of the Twelve Principles. In Table S4, we attempt to qualitatively assess how well each of these four case studies address the Twelve Principles.

Table S4. Evaluation of four (near) circular hydrometallurgical flowsheets in terms of the Twelve Principles of Circular Hydrometallurgy

Principle of Circular Hydrometallurgy	Case-study 1: Solvent extraction electrowinning (SX-EW) process in copper metallurgy	Case-study 2: Metallurgie Hoboken-Overpelt (MHO) process for ocean nodules	Case-study 3: Schnabel process for zinc extraction	Case-study 4: Molycorp's rare-earth extraction process
#1 Regenerate reagents	+++	+++	+++	+++
#2 Close water loops	+++	+++	+++	+++
#3 Prevent waste	+++	+++	++	++
#4 Maximize mass, energy, space and time efficiency	+	+	+	+
#5 Integrate materials and energy flows	++	++	+++	+++
#6 Safely dispose of potentially harmful elements	?	?	?	?
#7 Decrease activation energy	?	?	?	?
#8 Electrify processes wherever possible	++	-	-	++
#9 Use benign chemicals	+	+	++	+
#10 Reduce chemical diversity	+	+	++	++

#11 Implement real-time analysis and digital process control	?	?	?	?
#12 Combine circular hydrometallurgy with zero-waste mining	++	-	-	+
Remaining weaknesses and required improvements in terms of "ideal" Circular Hydrometallurgy	Only circular for Cu; Valuable trace elements are often not recovered; Chalcopyrite is difficult to process	HCl is regenerated by pyrohydrolysis; Working with Cl_2 gas requires special safety measures; Only intermediates are produced	Cannot be applied to sulfidic zinc concentrates and zinc ferrite (franklinite) without pretreatment; Only intermediates are produced	Difficulties with membrane fouling; conventional SX is used for REE separation; fossil fuel is used as energy source

+++ Very well addressed; ++ Well addressed; + Addressed to some extent; - Not addressed/ not relevant; ? No information available

Solvent-extraction–electrowinning (SX-EW) process in copper metallurgy (1)

The solvent-extraction–electrowinning (SX-EW) process, sometimes referred to as the *leach solvent-extraction electrowinning* (L-SW-EW) process, represents the industrial benchmark for the extraction of copper from oxidic ores, because of its simplicity, elegance and small environmental footprint [4] [5] [6]. The process flowsheet is an almost completely closed cycle and, in theory, only copper oxide and electrical power are required to produce ultrapure copper metal. The flowsheet is composed of three interconnected closed circuits: the leaching, solvent extraction, and electrowinning circuits. See Figure S1 for a schematic representation.

In the leaching circuit, dilute H_2SO_4 is used to solubilize the copper present in the oxidic ores via heap leaching. The *pregnant leach solution* (PLS) contains 1–6 g L^{-1} Cu and 0.5–5 g L^{-1} H_2SO_4, as well as dissolved impurities (Fe, Al, Co, Mn, Zn, Mg, Ca, *etc*.). These solutions are too dilute in terms of copper and too impure for the direct electrowinning of pure copper metal. Therefore, the PLS is first sent to the

extraction circuit. Solvent extraction (SX) purifies and concentrates the PLS, producing an electrolyte that is suitable for electrowinning. In the extraction step, the copper is selectively loaded into an organic solvent, which contains a chelating extractant that selectively reacts with copper rather than the other metal cations present in the PLS. Typically, these are commercial ketoxime/aldoxime extractants (LIX® or ACORGA® family). For each extracted Cu^{2+} ion, two protons are transferred to the aqueous phase. In this way the aqueous phase is returned to its original acidity and the raffinate is recycled to the leaching step of the process. In the stripping step, copper is stripped from the loaded organic solvent by the depleted electrolyte to form the *advance electrolyte* (> 45 g L^{-1} Cu) from which the copper is electrowon. The stripped organic solvent is then recycled to the extraction step. In the electrowinning (EW), Cu^{2+} ions in the advance electrolyte are reduced to copper metal at the cathode by a DC electrical current. H_2SO_4, produced at the anode of the electrowinning cell, is returned to the SX circuit in the Cu-depleted, spent electrolyte. There, it is reused to strip the Cu from the loaded organic solvent, converting it back to the advance electrolyte. The overall reaction of the entire SX-EW process is that copper oxides are transformed into copper metal.

The protons that are consumed in the leaching step are regenerated in the electrowinning circuit by oxidizing the water at the cathode to oxygen gas, with the associated release of protons to the solutions. Via the SX circuit, the protons are transferred from the electrowinning circuit to the leaching circuit. The only waste produced by the process are the barren rocks that are left behind as tailings after the copper has been extracted from the ore by heap leaching. Although these tailings are visually not very appealing, they are physically and chemically stable and their storage does not pose environmental risks. Gypsum is formed as a secondary mineral if the copper deposit contains calcium-rich gangue minerals.

Although an SX-EW flowsheet for copper recovery and refining appears fully circular at first sight, we must realize that only the copper is recovered in the basic configuration of the flowsheet and none of the valuable trace elements that might be present in the copper ore (*e.g.*, gold, silver, tellurium and cobalt) are valorized. This is a substantial disadvantage, deviating from the multi-metal mining paradigm discussed above. One possibility to address this issue is by creating a bleed stream that can be further processed for the recovery of these other metals, as is in the recovery of cobalt from Co-containing copper ores [7]. New flowsheets that are based on the direct leaching of chalcopyrite should certainly address the issue of trace-metal recovery. The process is only of a closed-loop nature for copper; the H_2SO_4 consumed in a reaction with impurities in the ore should be compensated by addition of a make-up acid.

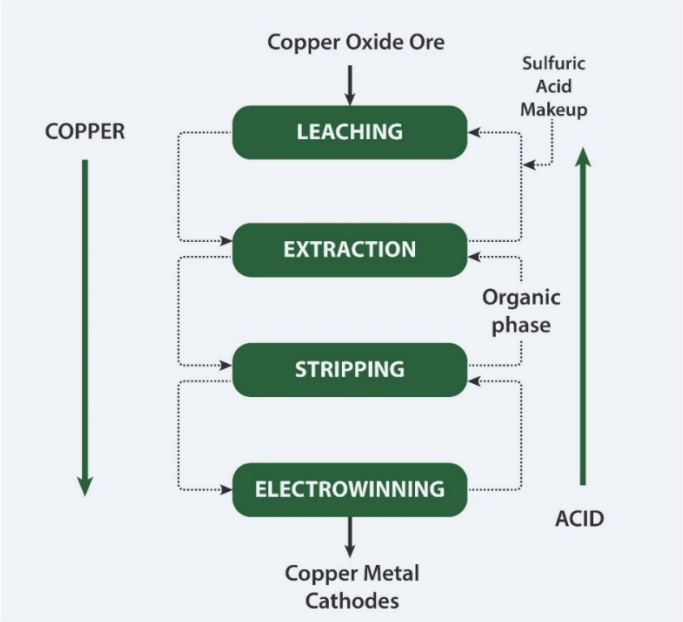

Figure S1. Schematic flowsheet of the leach – solvent extraction – electrowinning (L-SX-EW) process for recovery of copper from oxidic ores. Adapted after [4].

Metallurgie Hoboken-Overpelt (MHO) process for ocean nodules (2)

In the 1970s the Belgian company Metallurgie Hoboken-Overpelt (MHO, now Umicore) developed an elegant HCl-based circular flowsheet for the extraction of valuable metals from manganiferous ocean nodules (Figure S2) [8] [9] [10]. These nodules are mainly composed of MnO_2, with smaller amounts of hydrated iron oxides. They also contain significant levels of Ni, Co, Cu, Zn, V and Mo. These metals do not occur in discrete mineral phases, but are incorporated into the crystal lattice of the major metal oxide components, so that the nodules must be chemically treated in their entirety for trace-metal recovery. In the MHO process, the nodules are first crushed, and then leached directly in HCl. The acid is sufficient to reduce the manganese from MnO_2 to the soluble divalent state, forming $MnCl_2$ with the release of Cl_2 gas. Leaching is performed with concentrated HCl at elevated temperatures in a counter-current leaching setup of up to six leaching stages. The pregnant leach solution is a mixture of $MnCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$ and $CuCl_2$ (and Ca, Mg, V, Mo and Zn impurities) at a pH of 1 to 2. A great advantage of direct HCl leaching

is that the moist nodules do not have to be dried prior to leaching (in contrast to pyrometallurgical methods). However, as equation (4) shows, approximately 50% of the HCl is oxidized to Cl_2 gas during leaching. The Cl_2 must either be sold as a by-product or reconverted to HCl by reacting it with H_2 gas.

The MHO flowsheet offers an elegant solution to Cl_2 disposal. The Cl_2 from the leaching reactors is passed to the end of the process, where it is used to oxidize the $MnCl_2$ end-solution. Under conditions of controlled pH, obtained by neutralizing with MgO, manganese is precipitated from solution as a mixture of manganese oxides, while chlorine is reduced back to chloride. This enables the regeneration of HCl from the demanganized solution by the pyrohydrolysis of $MgCl_2$. The purification of the crude chloride liquor involves solvent extraction and several precipitation steps; it allows for the full recovery of the valuable metals contained in the manganese nodules. It is claimed that the following metal recovery yields can be achieved: Mn (99.9%), Ni (99.9%), Co (99.5%), Cu (99.9%).

The MHO process is an almost completely closed cycle. The only material inputs are the nodules; H_2S gas for precipitation of CuS, NiS and CoS; and some HCl to make up for the inevitable losses, as well as some small amounts of NaOH to process Mo and H_2SO_4 to process the pyrohydrolysis residue. All the other reagents are internally regenerated and reused. All the metals that are present in significant concentrations in the nodules leave the process either in usable or easily disposable form. Although this is an elegant flowsheet, the energy consumption is still relatively high due to the pyrohydrolysis step for HCl regeneration. It must be mentioned that this process produces intermediates (CoS, NiS, CuS, Mn oxides) that need to be further refined to final products. Although Cl_2 is considered as a toxic chemical and its release to the atmosphere must be strictly controlled, it can be handled safely in an industrial environment with closed reactor systems.

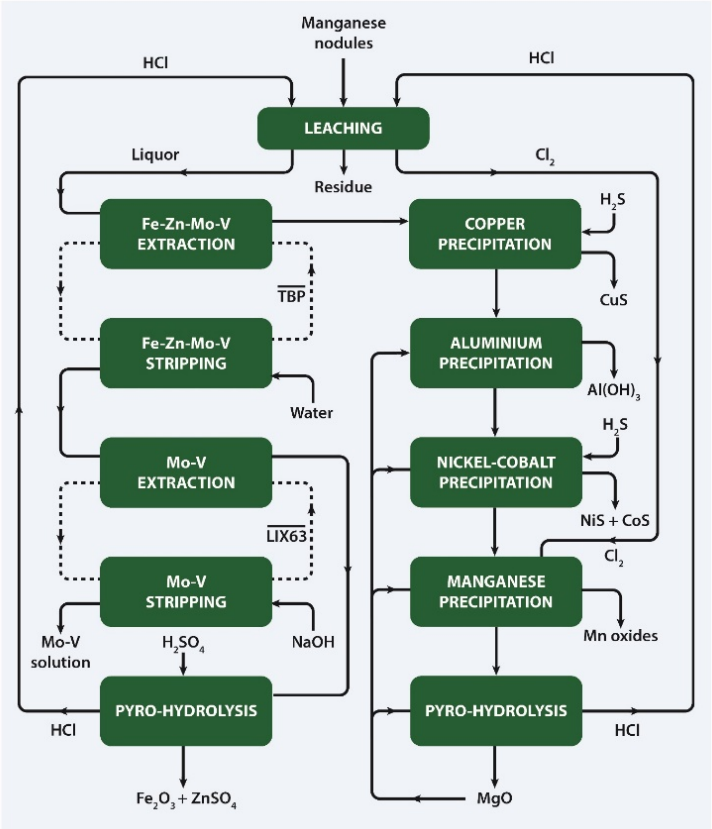

Figure S2. Circular flowsheet of the MHO process for the recovery of valuable metals from ocean nodules. Adapted from [10]

Schnabel process for zinc extraction (3)

Though the extraction of zinc using mixtures of ammonia solution and ammonium carbonate, the *Schnabel process*, is one of the oldest hydrometallurgical processes, many of its features are in accordance with the principles of circular hydrometallurgy. It was first described in the literature by Carl Schnabel in 1880, although at that time two operational plants already utilized the process. A schematic flowsheet of the Schnabel process is shown in Figure S3 [11]. The process can be directly applied to oxidic zinc feeds such as zincite (ZnO), hydrozincite ($Zn_5(CO_3)_2(OH)_6$), smithsonite ($ZnCO_3$), hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$), and the mixture of secondary zinc minerals called "*calamine*". It is also applicable to zinc-rich industrial process residues such as *Electric Arc Furnace* (EAF) dust and Waelz oxides, although not to the zinc ferrite (franklinite) fraction present in these materials. The process is not directly usable

on ZnS concentrates; these must be pre-treated by roasting. The core of the Schnabel process is the leaching of zinc from zinc-bearing materials by an ammonia-rich ammonium carbonate solution. The zinc is solubilized due to formation of soluble zinc ammine complexes. The exact speciation of the zinc complexes depends on the conditions used for the process, which has excellent selectivity for iron if the iron is present in ferric form. Ferrous iron is solubilized, but can be removed from the leachate by aeration of the solution to oxidize the ferrous ions, followed by the precipitation of $Fe(OH)_3$. Impurities of metals that are more noble than zinc (*e.g.*, lead and cadmium) can be removed from the solution by cementation with zinc powder. Zinc is precipitated from the purified leach solution as a basic zinc carbonate by steam heating. During this process, the excess of NH_3 is driven out and $(NH_4)_2CO_3$ is thermally decomposed to NH_3 and CO_2. The NH_3 and CO_2 gases are recovered and recombined to form a new lixiviant.

The Schnabel process offers many advantages [11]. The process is simple and economical. The ammonia – ammonium carbonate lixiviant can be completely recycled. Mild reaction conditions are required and the leaching reaction is fast; typically less than one hour is required for a complete reaction of a batch. Metal ammine complexes have a high solubility in this reaction system, allowing high zinc concentrations in solution and, hence, smaller leaching reactors. The process is selective for iron, and high-purity zinc solutions can be obtained, largely devoid of iron, lead, cadmium, copper, manganese, and silicon. The precipitation of basic zinc carbonate from solution is straightforward and requires limited process control. The process is robust in the sense that no precise adjustment of the lixiviant concentration or of the $NH_3/(NH_4)_2CO_3$ molar ratio is required. Conventional construction materials can be used, and corrosion problems are very limited. The Schnabel process is compatible with strict environmental regulations and near-zero effluent control is possible. The water requirements for the process are low, while the solid residue obtained after leaching is clean and might be used as a raw material for building materials.

The main disadvantage of the process is that it is not applicable, without a thermal pre-treatment step, to sulfidic zinc ores and spinel-type materials such as franklinite ($ZnFe_2O_4$). Another disadvantage is that the final product from the process is zinc oxide and not zinc metal, although research has investigated the direct recovery of zinc by electrowinning from an ammoniacal solution. Still, the Schnabel process has the potential for further development to treat zinc-rich residues from the steel industry [12] [13]. Furthermore, NH_3–$(NH_4)_2CO_3$ leaching offers opportunities for the sustainable recovery of copper, nickel, and cobalt from oxidic ores [14].

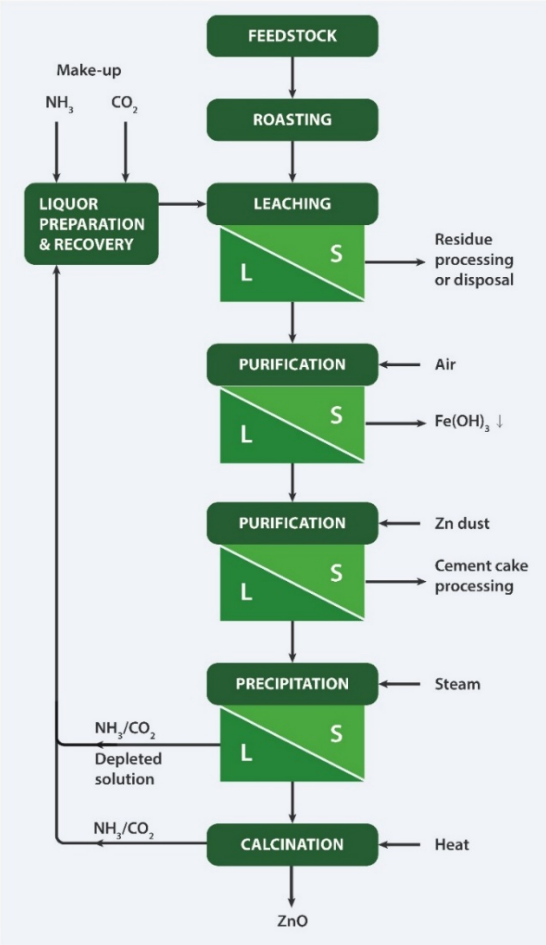

Figure S3. Circular flowsheet of the Schnabel process, including a roasting step for the pre-treatment of zinc sulfide concentrate. Adapted from [11].

Molycorp's rare-earth extraction process (4)

The Project Phoenix facility of the former REE-mining company Molycorp at the site of the Mountain Pass Mine in California (USA) is a good example to illustrate several of the principles of circular hydrometallurgy [15]. The aim was to develop a cyclic process for the efficient production of REEs from bastnäsite ore, while simultaneously reducing the disposal of wastewater. The project was advertised as an "integrated cradle-to-cradle reagent-and-water" solution using the most energy-efficient and clean sources for power. It was presented as an alternative for the once-through philosophy of conventional hydrometallurgy, *i.e.*, as an alternative for linear hydrometallurgical flowsheets (Figure S4). The core of

the Mountain Pass facility is a combined heat and power plant running on natural gas, producing both electricity and steam. The steam is required for process steps that require an elevated temperature such as the leaching step and in some parts of the solvent-extraction process. Although natural gas is a fossil fuel, it was considered much cleaner than the high-emission diesel, propane and "*bunker fuel*" that had been used previously on site. The older REE processing operations at Mountain Pass depended upon vast amounts of freshwater, which were locally sourced underground. This was problematic in a mountainous desert region such as the Mojave Desert, where Mountain Pass is located. Large amounts of wastewater were also produced. Most of the process water was consumed during the beneficiation of the bastnäsite ore, involving crushing, grinding, milling and froth flotation. In the cyclic process, the process water of the beneficiation and hydrometallurgical flowsheets can be recycled and the only freshwater that must be added is to compensate for losses by evaporation, occlusion in the solid phases formed in the process, and losses in the form of steam. In the Mountain Pass process, roasted bastnäsite ores are leached with HCl to solubilize the REEs. NaOH is used to neutralize the excess HCl and for pH control during the leachate-purification and solvent-extraction steps. The HCl and NaOH consumed in the process create a salt-water process stream that is meant to be recycled in the salt-recycling plant. This is a chlor-alkali plant in which the NaCl brine is reconverted into HCl, NaOH and NaOCl. In the electrochemical process, a NaOH solution and H_2 gas are produced at the cathode and Cl_2 gas at the anode. The anode and cathode compartments are separated by an ion-exchange membrane. Part of the NaOH reacts with Cl_2 to form NaOCl. In an "acid burner", the H_2 and Cl_2 react to form HCl gas. HCl, NaOH and NaOCl can be reused in the process or sold on the market. The recycling of the chemicals largely eliminates the need for 15 to 25 truck deliveries of chemicals per day. Still, the chlor-alkali plant caused many problems in the Phoenix project, mainly due to the impure brine that was produced during the processing of the bastnäsite ore. The main impurities in the brine were fluoride, sulfate, and divalent and trivalent metal ions. Following Molycorp's bankruptcy in 2017, the Mountain Pass mine was acquired by MP Materials. The mine has been reopened and in 2020 produced a total of 38,500 metric tons of REE concentrate (that is processed in China). The downstream processing and separation facilities are expected to restart in 2022, with a focus on the production of a neodymium-praseodymium mixture (NdPr, didymium) that can directly be used for permanent-magnet production (*vide supra*). On its website, the company is highlighting the sustainability of its near-zero-discharge operations [16].

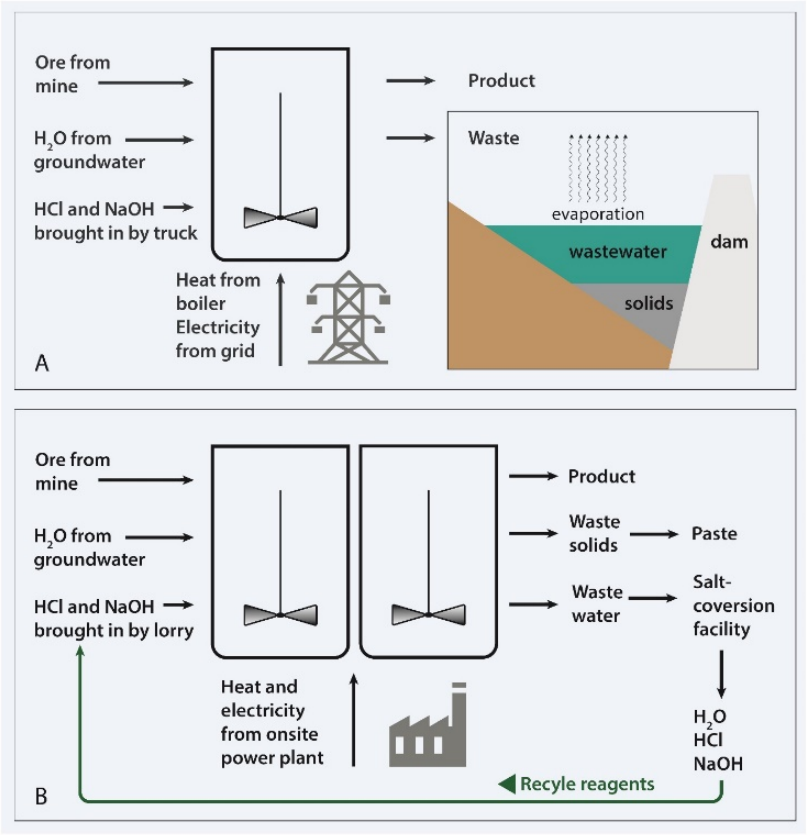

Figure S4. Schematic illustration of the (a) once-through approach compared to the (b) new cradle-to-cradle recycling approach at the Mountain Pass facility. Adapted from [15].

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