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ELECTROCHEMICAL RECYCLING OF RED GYPSUM WASTE: THE ELEDGE PROCESS

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Abstract

Red gypsum is an industrial waste generated by the titanium dioxide industry. Currently, it is mainly used for environmental restoration, but this is not ideal due to problems of geographical availability of suitable sites and environmental issues. Different valorization routes have been proposed, including the utilization of red gypsum in the cement industry or its chemical recycling through thermal processes. These routes either lack the production capacity for an efficient disposal of red gypsum, or propose processes that need severe operating conditions and that generate a significant amount of CO₂ emissions. This paper proposes a novel process for electrochemical recycling of red gypsum based on four fundamental steps: metathesis, electro dialysis, electrolysis, and carbonation. Preliminary estimates on a process design basis are obtained and analyzed from a phenomenological point of view, leading to the development of mass and energy balances for the process. The advantage of such system is that an industrial plant capable of treating 80000 t/y of CaSO₄ on an anhydrous basis leads to the production of 55234 t/y of concentrated H₂SO₄ and 52571 t/y of synthetic CaCO₃, coupled with the mineralization of 23131 t/y of CO₂. The process is completely electrified and has a power consumption of 8.5 MW that can be provided entirely from renewables-based power plants, leading to net-negative CO₂ emissions. Tuscany region in Italy is taken as a practical example, where the TiO₂ production industry could benefit from the ELEDGE (ELEttrodialisi di GEssi) process and couple it with a geothermal-based power plant.

Key words: electrochemistry, electro dialysis, recycle, red gypsum, Tuscany

Received: May, 2023; Revised final: June, 2023; Accepted: September, 2023; Published in final edited form: October, 2023

1. Introduction

Worldwide production of titanium minerals in 2022 was estimated at more than 9.5 Mt of equivalent titanium dioxide (TiO₂) content, with China covering more than one third of the mining operations (Statista, 2023). Titanium-containing minerals are included in the so-called “mineral sands” and include ilmenite and rutile, that make up the main feedstock for the industrial production of TiO₂, along with titanium slug. More than 95% of the world’s titanium ores are used in TiO₂ production, which is a key compound in the pigment industry. TiO₂ white pigments are mainly used in the paint, plastics, and paper industries, and also in wastewater treatment (Enesca et al., 2009;

Gázquez et al., 2014; Porter, 2014; Woodruff et al., 2017; Zarogiannis et al., 2017).

Nowadays, two large-scale industrial processes are available for the synthesis of TiO₂, those being the sulfate process and the chloride process. The increasing popularity of the chloride process is due to its higher performances regarding waste disposal, energy, and quality (Braun et al., 1992). However, the sulfate process is still dominant in China and it is also used for a significant fraction of the European TiO₂ supply chain, with 55% of the total still based on this technology in 2017 (Zarogiannis et al., 2017). The sulfate process includes a filtering and washing step that generates a weak acid effluent that is neutralized by using calcium hydroxide, leading to the production

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of a byproduct named “red gypsum” (Gázquez et al., 2021).

Red gypsum is mainly composed of gypsum dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and other impurities, among which Fe-bearing phases cause the typical red color. The management of this waste is a significant issue for the TiO_2 industry, since it is produced in large amount and has typically no practical use: 7-8 tons of red gypsum are generated for every ton of TiO_2 produced, and the most widespread use for this waste is the environmental restoration of abandoned quarries, mines, and landfills since it is considered an inert and safe material for such purpose (Auer et al., 2017; Protano et al., 2020; Rosli et al., 2020, 2021).

The utilization of red gypsum for environmental restoration may lead to the accumulation of species such as Fe, Ca, Al, Mg, Mn, S in the soil together with an increase of the pH of the area, leading to a slow and complicated revegetation process (Zapata-Carbonell et al., 2019).

Studies have shown that it is possible to use red gypsum to create a waste-based binder to be used in deep in-situ soil stabilization instead of cement, or it can be used directly as a raw material for cement production (Gázquez et al., 2013; Hughes et al., 2011). It has been also proposed to use this waste as a calcium-rich feedstock to be used for the mineralization of CO_2 , leading to the possible long-term sequestration of CO_2 -rich effluents derived from industrial processes with the formation of CaCO_3 (Azdarpour et al., 2014, 2015; Rahmani et al., 2014).

Finally, some solutions that may be classified as chemical recycling have been proposed, one example being the utilization of red gypsum as the pivot of a metal self-enrichment process leading to the co-production of ammonium sulfate and raw materials for the sintering industry (Wu et al., 2019) and another example being a thermal process for the conversion of red gypsum to elemental sulfur and calcium carbonate (De Beer et al., 2014).

The use of red gypsum in the cement and construction industry has a limited scope since the rate of utilization for this waste is subordinated to the production volume of said industry. Moreover, the amount to be used in this area is not arbitrarily large, due to constraints regarding the mechanical and chemical properties of the cement and ligands that are obtained from the gypsum. The chemical recycling route is a far more promising one, since it is disconnected from other industrial sectors and allows to selectively tackle the issue of red gypsum by converting it into useful chemicals. However, the solutions proposed in the literature are few and show some issues, such as the presence of severely endothermic steps such as calcination and thermal reduction that require temperatures above 1000°C , leading to the generation of large amount of CO_2 emissions from fossil fuels combustion.

This paper proposes a novel approach to this problem based on a completely electrified scheme for the electrochemical recycling of red gypsum. This innovative process solution is named ELEDGE

(ELEttrODialisi di GEssi, which means Gypsum ElectroDialysis in Italian) and it is based on four fundamental steps: metathesis, electroDialysis, electrolysis, and carbonatation, which lead to the complete conversion of red gypsum to diluted sulfuric acid and calcium carbonate. The electrification of the process allows to couple it to a suitable renewables-based power production plant, leading to a net-negative process for what concerns carbon emissions due to the mineralization of a CO_2 stream.

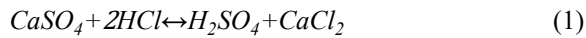
2. Materials and methods

A simplified Block Flow Diagram for the ELEDGE process is shown in Fig. 1, with electrified units highlighted by a lightning symbol. The conversion pathway for red gypsum is here shown only for the main component in its dehydrated form for simplicity (CaSO_4). The process is based on four tailored key steps aimed at converting the waste to useful products. First, red gypsum is co-fed with an excess of a concentrated hydrochloric acid solution (HCl) in a dedicated metathesis reactor, leading to the conversion of gypsum to sulfuric acid (H_2SO_4) and calcium chloride (CaCl_2). Then, the acidic mixture is treated in an electroDialyzer, a unit in which an electric field is applied to separate ions in solution by also exploiting suitable ion-selective semi-permeable membranes, producing a stream of diluted sulfuric acid and some brine rich in HCl and CaCl_2 . The excess HCl used for the metathesis step is easily separated and recirculated to the beginning of the process, while the CaCl_2 solution enters a dedicated electrolytic cell. The electrolysis of the CaCl_2 aqueous solution generates a calcium hydroxide (Ca(OH)_2) concentrated stream and gaseous hydrogen (H_2) and chlorine (Cl_2). H_2 and Cl_2 react in a dedicated unit (HCl burner) where HCl is generated and recirculated back to the beginning of the process, thus closing the HCl loop and ensuring that no net consumption of this reactant is necessary to run the process. Finally, the Ca(OH)_2 solution is used in a carbonatation reactor to mineralize a CO_2 stream (possibly obtained from a suitable stream of industrial flue gases), converting it into CaCO_3 . While introducing a new, innovative, and general approach for the chemical recycling of red gypsum that can be applied to any TiO_2 production facility, the technology is especially useful for the TiO_2 plant located in Scarlino, Tuscany, Italy. In fact, the production plant is close to a facility that produces sulfuric acid to be used in the sulfate process. Thus, it is possible to imagine an industrial symbiosis scheme in which red gypsum is treated with the ELEDGE process to produce diluted H_2SO_4 which can then be easily concentrated with the equipment available at the nearby sulfuric acid production plant, maximizing the efficiency of the chemical recycling operation and minimizing the costs and the energy requirements. In addition, the carbonatation reaction allows to mineralize CO_2 emissions that can be obtained from industrial off-gases, leading to the reduction of GHG emissions of the site. Moreover, the production of

synthetic CaCO_3 can partially substitute the intensive marble quarrying activity for the extraction of natural CaCO_3 that is currently conducted in the nearby Massa-Carrara area in Tuscany, Italy. This allows to mitigate the problem of marble powder generated by such activities, which turns into marble sludge in case of rainfall (the so-called “marmettola”), and may lead to environmental issues such as flooding and groundwater pollution (Piccini et al., 2019). Finally, it is also reasonable to imagine a possible coupling of the electrified ELEDGE process with a geothermal-based renewable energy power plant since this type of technology is well-established and popular in many areas of Tuscany region (Reinsch et al., 2017).

More detailed information on the process are shown in the Process Flow Diagram (PFD) in Fig. 2. It is possible to see that the system is a combination of the key operations described previously (metathesis, electro dialysis, electrolysis, carbonation) and a series of conventional steps, such as filtration, absorption, distillation, evaporation, purging. The process design solution proposed in this paper will proceed with the description of the key steps, without entering the detail of more conventional operations since they are well-known and a detailed evaluation of their performance is outside the scope of this work.

The metathesis step can be carried out in a stirred tank reactor in which red gypsum (rich in CaSO_4) and a concentrated solution of hydrochloric acid react according to the reaction shown in (Eq. 1):



The insoluble residue remaining from the metathesis step is filtered out of the system, then the sludge is washed with distilled water to recover water-soluble components, and the resulting solution is recirculated to the process vessel. It is possible to evaluate the performance of this reactive step through a thermodynamic evaluation by using Gibbs free energy and formation enthalpy of the involved chemical species, to be considered as dissolved in aqueous solution (Lange, 1999). The computation of reaction enthalpy and reaction Gibbs free energy at standard conditions highlights two values that are

close to zero ($\Delta H^0_R = -1 \text{ kJ/mol}$ and $\Delta G^0_R = -0.08 \text{ kJ/mol}$). This means that in this reaction, neither the reactants nor the products are favored, and that variations in the operating temperature will have little to no effect on the thermodynamic yield. In order to push the reaction towards the products and ensure high conversion of the gypsum, it is necessary to operate on other parameters, for example by working in large excess of hydrochloric acid. Equilibrium can be studied for this system by solving the system of equations in (Eq. 2), respectively showing the equilibrium condition and the Van't Hoff equation. Since the reaction enthalpy at standard conditions shows a rather small value, the computation of the Van't Hoff equation is performed by considering a constant value for ΔH^0_R , leading to the expression shown in (Eq. 2).

$$\begin{cases} K_{eq}(T) = \prod_{i=1}^N a_i^{v_i} \\ K_{eq}(T) = K_{eq}(T_{REF}) \cdot \text{EXP} \left[\frac{\Delta H^0_R}{R} \cdot \left(\frac{1}{T_{REF}} - \frac{1}{T} \right) \right] \end{cases} \quad (2)$$

where K_{eq} , T , N , a_i , v_i , T_{REF} , ΔH^0_R , R , are respectively the equilibrium constant, the system temperature, the number of components, the activity for the i -th component, the stoichiometric coefficient for the i -th component, the reference temperature (298 K), the reaction enthalpy, and the universal gas constant.

The CaCl_2 -rich brine containing two strong acids (H_2SO_4 and HCl) is then sent to an electro dialyzer. Electro dialysis is a process which is typically used to perform water desalination and salt pre-concentration. It works by applying an electric field to an ionic solution contained inside of a space delimited by anion- and cation- exchange membranes. The electric field combined with the selectivity of the membranes allows to separate the dissolved ions (Strathmann, 2010; Xu and Huang, 2008). There are also innovative approaches based on electro dialysis such as bipolar membrane electro dialysis for the production of acid and bases from corresponding salts, showing that this technology can potentially be applied to a large number of cases in addition to that of water desalting (Huang et al., 2007).

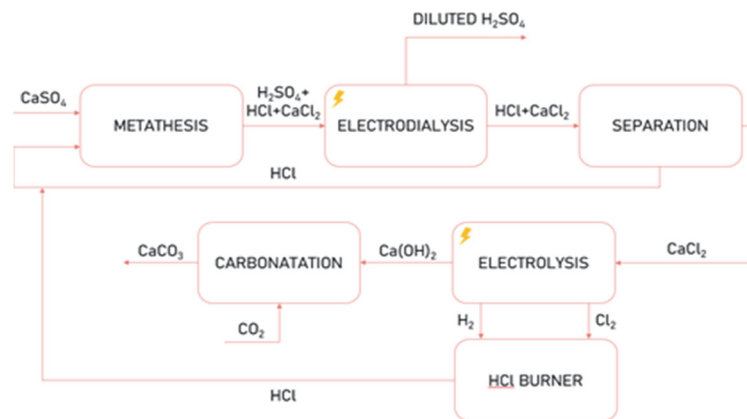


Fig. 1. Block flow diagram for the ELEDGE process

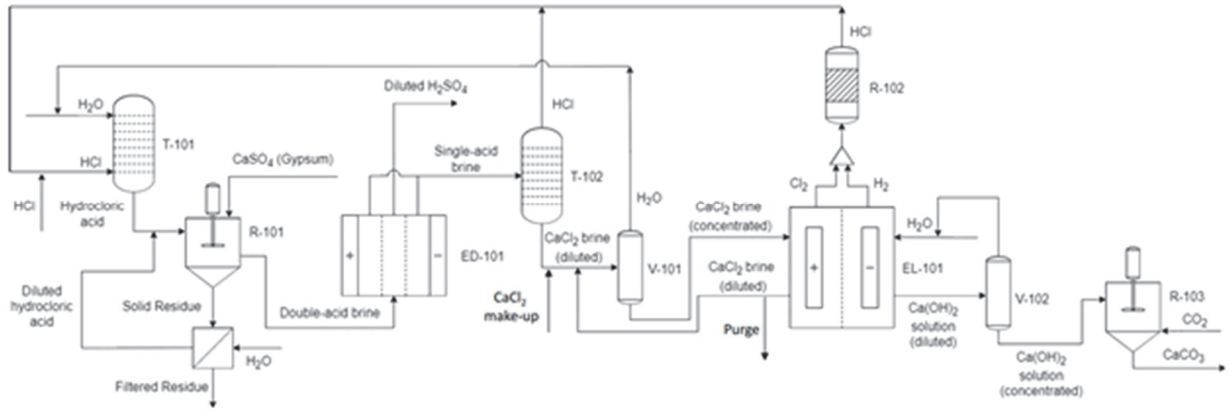


Fig. 2. Process flow diagram for the ELEDGE process

It is interesting to notice that it is possible to use an ion-selective anion-exchange membrane so that a separation between different anions in solution can be achieved on top of the more conventional cation/anion separation. Specifically, it has been shown that it is possible to use semi-permeable membrane for the selective separation of Cl^- and SO_4^{2-} anions (Li et al., 2022). A simplified scheme of an electrodesialyzer using this type of anion-selective membrane for the treatment of the CaCl_2 -rich double-acid brine is shown in Fig. 3. The double-acid brine containing CaCl_2 , HCl , and H_2SO_4 is fed to the unit and the cations start to migrate towards the cathode by passing through a cationic membrane, while the anions tend to migrate towards the anode by passing through an anionic membrane. However, the use of a $\text{Cl}^-/\text{SO}_4^{2-}$ anion-selective membrane makes it much more difficult for the larger sulfate ions to pass through the membrane, allowing almost only the Cl^- ion to pass. This leads to the production of diluted sulfuric acid from the central channel, and a single-acid brine containing HCl and CaCl_2 from the sides. While the cation/anion separation can be considered as practically complete, the separation efficiency for the anion-selective membrane is not perfect (Li et al., 2022). This is not a problem for the diluted sulfuric acid stream, since it will contain a small amount of HCl easily separable by distillation, due to the very different boiling points of these substances between themselves and water. However, this may generate a problem for the single-acid brine since the leaching of sulfate ions will regenerate CaSO_4 that cannot be re-converted to CaCl_2 in the following process steps. To avoid its accumulation, it is either necessary to purge it outside of the system and compensate the loss of material with a fresh CaCl_2 make-up, or split the effluent from the electrodesialyzer and recirculate it to the metathesis section, where CaSO_4 will be converted to CaCl_2 . In this work showing the conceptual design procedure for the process, it has been decided to proceed with the first choice for the sake of simplicity, even if it is less optimal.

The single-acid brine containing HCl and CaCl_2 then undergoes a simple distillation to recover pure gaseous HCl from the top, to be recirculated to a water absorption column for the synthesis of the

hydrochloric acid solution that is used in the metathesis reactor. The brine, now only containing calcium chloride, is then concentrated and added with a CaCl_2 make-up before entering an electrolytic cell for the electrochemical decomposition of the salt. Inspired by the chloralkali process for the industrial production of chlorine and sodium hydroxide, the electrolysis step in the ELEDGE process includes the half-reactions reported in (Eq. 3). They are the same half-reactions that take place in the chloralkali process, those being the oxidation of chloride anions to chlorine at the anode, and the reduction of water to hydrogen and hydroxide anion at the cathode (Schmittinger et al., 2011). The only difference with the chloralkali process is that the cations in this system are Ca^{2+} ions, leading to the production of $\text{Ca}(\text{OH})_2$.

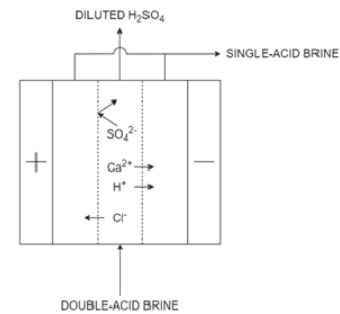


Fig. 3. Electrodesialyzer step in the ELEDGE process

It is possible to evaluate the performance of this electrochemical cell through a thermodynamic evaluation by starting from standard reduction potentials of the chemical species involved in each half-reaction and shifting them to the real operating conditions by using the Nernst equation, as reported in (Eq. 4).

$$E_{RED} = E_{RED}^0 - \frac{RT}{zF} \ln \left(\frac{a_{RED}}{a_{OX}} \right) \quad (4)$$

where: E_{RED} is the half-cell actual reduction potential, the E_{RED}^0 is the standard half-cell reduction potential, T is the system temperature, R is the universal gas

constant, z is the number of electrons transferred in the half-reaction, F is the Faraday constant, a_{RED} is the activity of the reduced form, a_{OX} is the activity of the oxidized form. A rigorous methodology should include suitable expressions for the activity coefficients of the species involved in the reactions (Thummar et al., 2022). However, it is possible to have a preliminary estimation of the reduction potential by considering the activity of a dissolved species as the concentration, and the activity of a gaseous product as its partial pressure. This is coherent with the preliminary level of the conceptual design procedure introduced in this work.

Chlorine and hydrogen gas produced from the atmospheric electrolytic cell must be compressed and fed to an HCl burner, where gaseous hydrogen chloride is produced through an extremely exothermic reaction, leading to the production of a substantial amount of steam to be used in the plant (Austin and Glowacki, 2000). HCl is then recirculated to the water absorption column to regenerate the 5 M hydrochloric acid solution, thus closing the HCl loop and ensuring that no net consumption of this reactant is needed to run the process.

Finally, the $\text{Ca}(\text{OH})_2$ solution produced at the cathode of the electrolytic cell is processed in a carbonation reactor, where CO_2 bubbled from the bottom is mineralized upon contact with the caustic solution, leading to the production of synthetic CaCO_3 (Boynton, 1980; Oates, 2008).

3. Results and discussion

The process design procedure described in this paper allows to choose the optimal operating conditions for the non-conventional unit operations included in the system, followed by a high-level mass balance for a plant based on the ELEDGE process. The thermodynamic study performed in the metathesis

step shows that the use of a 5 M hydrochloric acid solution at 80°C corresponds to a CaSO_4 conversion higher than 99%. The system temperature has a negligible effect on the thermodynamic yield, but the combination of HCl presence and the choice of operating temperature allows to maximize CaSO_4 solubility in the aqueous solution, leading to a great increment in the productivity of the unit. It must be noted that the co-presence of CaSO_4 and CaCl_2 generated from the metathesis decreases gypsum solubility. However, the choice of operating conditions results in a net increase in CaSO_4 solubility, passing approximately from 2 g/L to 20 g/L when referring to its anhydrous form (Li and Demopoulos, 2005). The effluent from the reactor to be purified in the electro dialysis unit is separated in a diluted sulfuric acid stream and a brine containing mainly HCl and CaCl_2 , with a separation efficiency that can be quantified as follows: 91.71% of the Cl^- ions and 5.44% of the SO_4^{2-} ions pass through the anionic membrane on average (Li et al., 2022). Finally, the brine concentration in CaCl_2 and the operating temperature chosen for the electrolytic cell are such that there is a deviation from the standard thermodynamic potential, and the resulting half-cell reduction potentials at the chosen operating conditions lead to an overall thermodynamic electrochemical potential of 1.94 V, which is 12% less than the standard overall thermodynamic potential (2.19 V). With these data, it is possible to perform a high-level mass balance for the system based on the ELEDGE process.

The size of the plant considered for the mass balance refers to an industrial complex capable of treating 80000 t/y of CaSO_4 on an anhydrous basis and that has a stream factor of 8000 h/y. The mass balance of the proposed layout, along with the main operating temperatures is reported in Table 1, where the stream names refer to the PFD shown in Fig. 2.

Table 1. Mass balance and operating conditions for the main streams of the ELEDGE process

Stream Name	CaSO_4	Hydrochloric acid	Double-acid brine	Diluted H_2SO_4	Single-acid brine	CaCl_2 brine conc.	$\text{Ca}(\text{OH})_2$ solution conc.	CO_2	CaCO_3
Phase	S	L	L	L	L	L	L	G	S
Composition [mol%]									
H_2O	89.4%	82.6%	85.9%	94.5%	78.7%	94.5%	99.976%	0%	89.3%
CaSO_4	7.89%	0%	0%	0%	0%	0%	0%	0%	0%
HCl	0%	17.4%	10.8%	1.96%	18.1%	0%	0%	0%	0%
CaCl_2	0%	0%	1.67%	0%	3.07%	5.38%	0%	0%	0%
H_2SO_4	0%	0%	1.67%	3.49%	0.17%	0.14%	0%	0%	0%
$\text{Ca}(\text{OH})_2$	0%	0%	0%	0%	0%	0%	0%	0%	0%
CO_2	0%	0%	0%	0%	0%	0%	0%	0%	0%
CaCO_3	0%	0%	0%	0%	0%	0%	0.024%	0%	0%
Inerts	0%	0%	0%	0%	0%	0%	0%	100%	0%
Flowrate [kmol/h]	932	3528	4361	1981	2381	4233	270221	66	613
MW [kg/kmol]	30	21	23	21	24	23	18	44	27
Mass Flowrate [kg/h]	27500	74884	99884	41896	57988	97945	4867655	2891	16428
Temperature [$^\circ\text{C}$]	25	80	80	25	25	80	80	80	80

The electric energy requirement for the process can be estimated by considering that the steam production from the HCl burner is sufficient to cover all the requirements from the other process units such as the metathesis reactor, the distillation column, and the evaporators. This means that the only electric power required to run the process refers to the electrodialysis and electrolysis steps. For the electrodialysis, a preliminary energy consumption for the system described previously can be obtained from the literature, corresponding to an average value of 0.20 kWh/kgCaCl₂ (Li et al., 2022). For the electrolytic cell, it is possible to consider the typical average values for current density and effective electrode area for a standard chloralkali cell, and refer them to the influent calculated for the industrial case, while considering the overall thermodynamic potential calculated as shown in (Eq. 4). The electrolytic cell resulting from the analysis has a specific power consumption of 0.27 kWh/kgCaCl₂ (Thummar et al., 2022).

Considering the industrial-scale plant operating with a capacity of 80000 t/y of CaSO₄ on an anhydrous basis, this corresponds to a power consumption of 1.6 MW for the electrodialysis, and 6.9 MW for the electrolytic cell, for a total of 8.5 MW. Thus, it is reasonable to imagine the erection of such an electrochemical recycling plant in the Tuscany region and power it completely through renewable geothermal energy since the total installed capacity for this type of renewables system in the region in 2023 is 915 MW provided by 33 power plants, with 20 MW to be installed in the following years (Regione Toscana, 2023). The resulting electrochemical recycling plant is effectively a net-negative carbon emissions process, with the utilization of 0.29 kgCO₂/kgCaSO₄ through mineralization.

4. Conclusions

The design of an electrochemical recycling process for red gypsum waste was described in its most important parts: metathesis, electrodialysis, electrolysis, and carbonatation.

A thermodynamic analysis was performed for the metathesis step in order to find the optimal operating conditions. An electrodialysis unit based on the use of a Cl⁻/SO₄²⁻ anion-selective membrane was illustrated in terms of separation efficiency and general performance, followed by the evaluation of the real overall thermodynamic potential of an electrolytic cell. The carbonatation section was introduced and described in detail.

The ELEDGE process can be used in an industrial plant capable of treating 80000 t/y of CaSO₄ on an anhydrous basis, obtaining, after suitable purification steps aimed at removing excess water and other contaminants, 55234 t/y of concentrated H₂SO₄ and 52571 t/y of synthetic CaCO₃, while also mineralizing 23131 t/y of CO₂, with an electric consumption of 8.5 MW that can be entirely provided

by renewables such as geothermal energy for the case of titanium dioxide industry in Tuscany region, Italy. The renewables-based electrochemical recycling process is a net-negative CO₂ emissions process, due to the mineralization of a CO₂-rich stream.

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