IDENTIFICATION AND EXPLOITATION POSSIBILITIES OF SOME WASTE PRODUCTS FROM ION EXHANGE MEMBRANE ELECTROLISYS PLANT

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Abstract: *The aim of this study consists in the identification of industrial waste products from ion exchange membrane electrolysis plant and their revaluation possibilities.*
Nevertheless this is a BAT process, after ion exchange membrane electrolysis brine results important quantities of inorganic sludges. At this moment, these wastes that contain $CaSO_4$, $CaCO_3$, NaCl, $Mg(OH)_2$, $Ca(OH)_2$ and heavy metals from NaCl bank or $CaCO_3$ used at salt solution chemical purification, are removed to waste dumps.
Waste dumps induce the modification of quality of environment components- ground, underground water and surface water- the decrease of these quantities meaning an important factor in environmental quality protection.

Keywords: *calcium chloride, sludge, heavy metals, ion exchangers.*

Introduction

Simultaneous produce of chlorine, hydrogen and caustic soda from aqueous solutions of alkaline metals in electrical applying is known as electrolysis of alkaline chlorides. There are many electrolytic processes, the most efficient (considering the power consumption) is the process with ion exchange membranes (MSI) (Szep A., Brandabur F., Minea I., 2002). **Prime matter,** the base in electrolytic process is sodium chloride. In the production process of these compounds there are also used other materials, such as: H_2SO_4, $CaCO_3$, Na_2SO_3, $CaCl_2$, ion exchange resins. **The products of electrolysis** that results in MSI process have height purity: electrolytic chlorine (98%), caustic soda (33%) and hydrogen (99%). The high quality of these products is due to the ion exchange membrane, but, its performance is conditioned by the purity of the electrolyte; that means that in the process the first matter phase purification is very important - sodium chloride solution, brine.

The brine purification takes place in two steps: first step consists in desulphurisation the solution and chemical precipitation of Ca^{2+} and Mg^{2+} ions; followed by the percolation on coal and cellulose filters; the second step is an advanced purification on cationic ion exchange columns.

Identification of waste products

We name waste products, any substance in solid or liquid phase that results in production process or home and social activities, that can't be used according with initial destination and necessitate special requirements in keeping or storage to be reused or to restrict noxious effects (Macoveanu, M, 2005).

In the technological diagram from brine purification, Fig.1, we can see the next sources of waste products:

- From first brine purification - after filtering - wastes that contain $CaSO_4$, $CaCO_3$, NaCl, $Mg(OH)_2$, impure water;
- From filtration of brine on cellulose filters, cellulose cake that contains $CaSO_4$, $CaCO_3$, NaCl, $Mg(OH)_2$;
- From washing/regenerating ion exchange columns, waters that contain $CaSO_4$, $CaCO_3$, NaCl, $Mg(OH)_2$;
- From washing/regenerating ion exchange columns- a small part of cationic resins are broken at regeneration, which takes place at the modification of the volume.

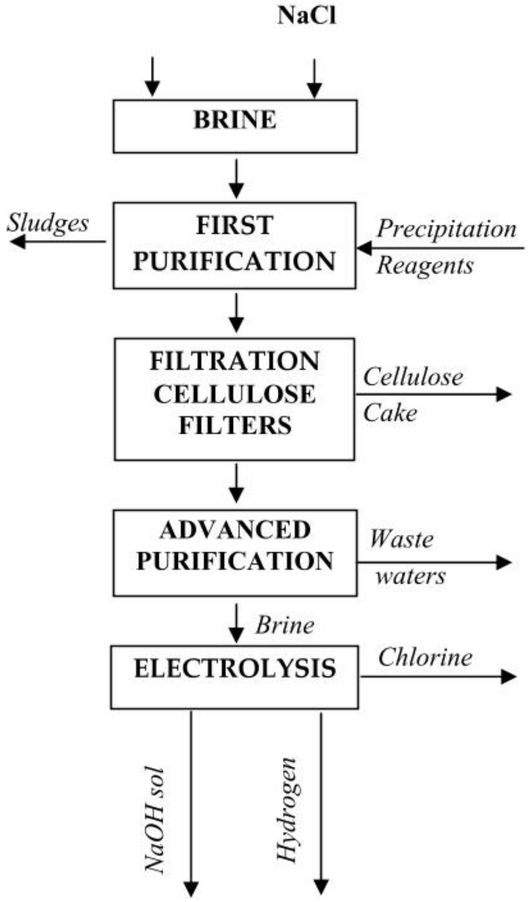

Figure1. Flow chart of the brine purification

As we can see, the most important waste products, as sludges, result in the first purification phase of brine, in chemical precipitation. These sludges consist in important quantities of $CaSO_4$, $CaCO_3$, NaCl, $Mg(OH)_2$, $Ca(OH)_2$ and heavy metals from NaCl bank or $CaCO_3$ used at salt solutions chemical purification; now, these sludges are removed to waste dumps and represent an important pollution potential.

Characteristics for the sludge from brine purification

In Tab.1 we can see some of the important characteristics of sludges from brine purification. We get the samples from waste dumps. As we can see, the sludge from brine purification have an important content in $CaCO_3$, above 60%, and so, this sludge is an important source of $CaCO_3$ that can be used to obtain other products. In addition to Tab.1, these sludges also contain heavy metals. We find the content of heavy metals using atomic absorption methods and Varian SPECTRA AA instrument.

The average values for our samples (Popa C., 2008) are: Cu^{2+} = 3.8ppm; Fe^{2+} = 240 ppm ; Cr^{3+} = 33.2 ppm; Pb^{2+} = 2.5 ppm; Cd^{2+} = 0.9 ppm; Zn^{2+} = 5.5 ppm; Ni^{2+} = 28.9 ppm; Sb^{3+} = 4.8 ppm.

Possibilities on exploitation of $CaCO_3$ from sludges

$CaCO_3$ contained in the sludge can be used in different manners, Tab.2, to obtain:
- calcium chloride;
- soda in Leblanc process;
- soda in Solvay process;
- calcium hypo chloride;

Table 2 Comparative analysis of the possibilities to recover the calcium carbonate from waste dumps

$CaCO_3$ USED TO OBTAIN SODA - LEBLANC PROCESS (Winnacker si Kughler, 1966), (Calistru C., Leonte C., 2006).	**$CaCO_3$ USED TO OBTAIN SODA - SOLVAY PROCESS** (Ullmann's, 1998), (Winnacker si Kughler, 1966), (Calistru C., Leonte C., 2006).	**$CaCO_3$ USED TO OBTAIN CALCIUM HYPOCHLORIDE** (Ullmann's, 1998), (Winnacker si Kughler, 1966).	**$CaCO_3$ USED TO OBTAIN CALCIUM CHLORIDE** (Calistru C., Leonte C., 2006), (Kirk-Othmer, 2001).
1) Equipment/special materials : Technological outline consists in 6 phases required to obtain the final product, soda, phases that impose technical problems using special equipments: - ovens for sulphate, resistance to acids; - burning ovens for fusion soda - installation for rapid dissolution and rinsing; - evaporating ovens; - washing towers for gases;	**1) Equipment/special materials :** Technological outline consists in 5 phases required to obtain the final product, soda, phases that impose technical problems using special equipments: - burning ovens; - horizontal spinning drummer for lime extinguish; - filled washing columns - absorption systems consist in columns with plates; - precipitation towers; - rotating filters; - burning ovens; - crack columns with plates; - reservoirs for decant waste solutions;	**1) Equipment/special materials :** - nourish bunker - transport band; - elevators - silo - Schultes systems - sieves - chlorination rooms - buffer tank for chlorine;	**1) Equipment/special materials :** - steel reaction vessel (OL37), rubber coated and diabaz coated; - pumps, transport band from V2A; - bunker, washing towers, electric fans made of usual materials; - decantation apparatus made of OL37, rubber coated; - neutralization tank, OL37, rubber coated; - store reservoirs, OL37, rubber coated;
2) Temperatures and pressures in exploitation: - for complete sodium chloride transformation into Glauber salt it is necessary an high calcinations temperature, to dark red (960 ^{0}C) ; - at raw soda obtained phase, from Glauber salt, coal and limestone, temperatures around 1000 ^{0}C are also necessary ; - at evaporation and calcinations of soda solution are necessary upper and lower furnace are necessary, with high temperatures;	**2) Temperatures and pressures in exploitation:** - disintegration of calcium carbonate to obtain carbon dioxide require high temperatures, up to 900 ^{0}C ; - transformation of bicarbonate to carbonate is made into burn ovens; - ammonia distilling with steam is made over atmospheric pressure;	**2) Temperatures and pressures in exploitation:** - the hydration water for lime is heated at 70-90 ^{0}C. - the temperature at chlorination room, 45 ^{0}C. - vacuum at chlorination room 10-15mm CA - steam for temperature correction at neutralize phase 160 ^{0}C, 4-6.5barri - industrial water for lime slake and for the correction of the temperature at chlorination rooms 5 - 28^{0}C, 3-4.5barri.	**2) Temperatures and pressures in exploitation:** - atmospheric pressure; - atmospheric temperature;
3) The security in operation:	**3) The security in operation:**	**3) The security in operation:**	**3) The security in operation:**

- HCl, corrosive liquid ; - fusions chemical and thermo aggressive; - HCl vapours- corrosive, toxic an irritant;	- carbon dioxide, toxic gas; - ammonia, toxic and irritant gas;	- chlorine, toxic and corrosive gas; - HCl steam, corrosive, toxic an irritant;	- HCl – corrosive liquid; - $CaCl_2$ before neutralisation – corrosive liquid;
4) Environment aspects: - HCl vapours in the air, corrosive and irritant compound for the organism; - large quantities of residuum as CaS_2, carbonate and coke – 1.5t residuum/tone of soda; - when storing waste products in waste dumps, disintegration takes place in the presence of air , with heat emitting; H_2S and SO_2 infect the atmosphere; - the waste products storage in waste dumps produce water pollution problems;	**4) Environment aspects:** - residual solution from ammonia distillation is not used, it can not be used in another process, and so, it is evacuated into water courses after separation and dilution; - the sludge that contain sulphate and calcium carbonate together with impurities from limestone can not be reused in another process, an so, is stored to waste dumps; - waste products from lime extinguish and the ash are ballasts for the plant;	**4) Environment aspects:** - the technology has an small impact for environment; results only waste waters from floor washing;	**4) Environment aspects:** Generally, the technology has an small impact for environment; results small quantities of waste waters from floor washing and from acidic gases washing- synthesis phase;
5) Assurance with raw materials; - H_2SO_4 is already available in a soda plant, as it is obtained in the process of waste sulphuric acid concentrating; - limestone comes from Constanta or Teius and will be supplemented or replaced with the limestone from electrolysis sledges;	**5) Assurance with raw materials;** - sodium chloride (as brine) is already available in a soda plant; - CO_2 source from limestone Teius and Constanta, or from electrolysis sludge.	**5) Assurance with raw materials;** - chlorine source is already available in a soda plant; - $CaCO_3$ source from limestone Teius and Constanta, or from electrolysis sludge;	**5) Assurance with raw materials;** - HCl 34% already available in a soda plant - $CaCO_3$ source from limestone Teius and Constanta, or from electrolysis sludge;
6) Logistics; - complete new and expensive investment to produce soda; - problems to solve pollution, transport and storage for wastes to waste dumps;	**6) Logistics;** - complete new and expensive investment to produce soda; - problems to solve pollution, transport and storage for wastes to waste dumps	**6) Logistics;** - the arrangement for a plant or use the existent one; - storage of raw matter;	**6) Logistics;** - the arrangement for a plant or use the existent one; - storage of raw matter;
7) Sale market : - unconquered, the plant is not a traditional producer for soda;	**7) Sale market** : - unconquered, the plant is not a traditional producer for soda;	**7) Sale market** : - already conquered for a traditional producer of $CaCl_2$;	**7) Sale market** : - already conquered for a traditional producer of $CaCl_2$;

Table 1
Characteristic parameters of sludge

Parameter content [%]	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Range
H_2O	16,82	18,2	14,4	18,3	18,23	14,4 – 18,2
SO_4^{2-}	1	1,6	1,2	1,8	1,3	1–1,8
$CaCO_3$	61,9	61,6	65,5	66	66,3	61 – 67
NaCl	6,9	,68	7,64	6,75	5,93	6 – 8
$Mg(OH)_2$	1,65	1,7	0,47	1,26	1.,2	0.5 – 2

In the options for exploitation of $CaCO_3$ in the technologies that we saw earlier, we considered as important the following factors:

- raw materials
- complexity of the process;
- necessary equipments and special materials;
- temperature and pressure;
- safety in operating;
- environment problems;
- sources of raw materials;
- logistics;
- commodity market;

If we compare the possibilities of exploitation for sludge $CaCO_3$, we can observe:

• In the case of obtaining soda in Leblanc and Solvay processes:

- the technologies are complicated, they have 5 or 6 phases ;
- use special equipments to resist at high temperatures and corrosion;
- manipulate solutions and fusions chemical and thermo aggressive.
- the technologies induce a serious environmental impact, resulting important quantities of residues that require to be destroyed or deposited, and also residual gases that infect the air.
- the investments are expensive for a company that is not a soda producer;
- the market is not discovered, for the same reason;

• In the case of obtaining calcium hypo chloride and calcium chloride:

- the technologies are not so complex;
- use equipments that are resistant to corrosion;
- the technologies have not an important environment impact, in the process of producing results only waste waters from washing processes- washing residual gases and washing concrete floors;
- are not necessary new investments, an soda producer has usually and a plant to produce calcium hypo chloride and calcium chloride
- the market is already conquered;

• In the case of obtaining calcium hypo chloride, there is a quality condition for $CaCO_3$, because there is a strong relation between granulation distribution of calcium hydrate and the content in active chloride; Because this fact, industrial $CaCO_3$ is broken to 40-60mm, and also at hydration phase, we adjust the quantities of water and $CaCO_3$ through the analytical control of the obtained hydrate, thus, it's humidity must be between 6-8%.

Also, a good quality limestone contains 95% CaO and less than de 2% MgO, 0.5% Al_2O_3, 1%SiO_2 (Ullmann's, 1998). These aspects are impediments in using the sludge as source of CaCO3 to obtain calcium hypo chloride;

In consideration for those that we explained, we can observe that the most suitable way to revaluate CaCO3 from electrolytic sludge is **to obtain calcium chloride** in reaction with hydrochloric acid.

Conclusions

The revaluated waste product from an MSI electrolysis plant is the sludge that results in the chemical purification process of brine; this sludge can be efficiently reused to obtain calcium chloride in reaction with hydrochloric acid. To ensure quality conditions, calcium chloride obtained through

this method can be purified in an exchange ion process, thus recovering the heavy metals (Dardel F., Arden T., 1998).
Through the recovery of $CaCO_3$ from electrolysis sludges as calcium chloride and purifying it to touch quality conditions of standards, we meet two objectives:
- we reduce the quantity of industrial sludges evacuated to the waste dumps solving in this way an environment problem;
- we obtain calcium chloride solution, an industrial product used in chemical industry, extractive industry, food industry, construction.

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