UNIVERSITY OF PETROȘANI

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RECOVERY AND VALORIZATION OF MINERAL SUBSTANCES AND USEFUL ELEMENTS FROM GREEN SLUDGES FROM INDUSTRY

~ SUMMARY ~

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INTRODUCTION

The concept of sustainable development in the management of mineral resources generally involves carrying out activities in such a way as to prevent damage to the environment and the quality of life in the areas concerned. The 'mountains' of tailings deposited in dumps, which have arisen as a result of a lack of interest in the comprehensive use of mineral resources, are a testimony to the fact that this has been ignored over the ages. All the measures adopted are justified by the - rather belated - recognition that our planet has a limited capacity to meet the growing demand for non-renewable natural resources from the socio-economic system and to absorb the destructive effects of their use.

Taking into account market developments, since 2011, the demand for metals has been steadily increasing due to their use in modern and cutting-edge technologies. Their exploitation has become an environmental concern, through the modification of ecosystems, pollution and waste generation, as well as end-of-life due to consumption and production, showing how important it is to rethink the use of natural resources by the economy and society, but also the need to conserve these resources for future generations.

In recent years, this circular economy concept and its related policies have widely addressed resource use, production, consumption and waste. The concept aims to close the material loop by keeping the value of products, materials and resources in the economy for as long as possible. This effectively reduces waste generation and assumes the use of raw materials, while achieving a reduction in associated pressures. [27]

The most important strategy to achieve this goal is to develop the economy into a "closed-loop" system of transforming matter and energy (flow-circular economy) without achieving ecological balances, by introducing waste into the loop and closing the waste flow.

Recycling waste under current legislation seems to introduce a maximum of 2/3% of waste into the production stream, with the remaining 1/3 forming waste from other waste, such as a technological stream (see here waste combustion). Thus we deduce that, for the time being, the waste-free society remains at the level of utopia.

We define waste as any material which, in its current form, can no longer be used. Any material (or object) defined as waste in the form in which it is, can become reusable after a series of transformations. It is therefore necessary to find ways of transforming and re-using as much primary waste as possible.

Waste arises from almost any type of activity and, depending on the source that generates it and gives it certain characteristics, it can be categorized into different groups according to certain criteria.

In conclusion, the materials industry and therefore the mining industry is faced with a limited number of options regarding: sustainable production processes, material recycling - technologies to improve waste collection, sorting, recycling and recovery, building new "industrial ecosystems", emerging technologies, i.e. associated smart contracts, blockchains, coherent policies to stimulate the circular economy.

However, most of these solutions are neither effective nor widely available.

Objective of the work: Undoubtedly, the main object of the valorization of green sludge, which is industrial waste deposited in huge landfills and containing polluting and harmful elements for the nearby population. All the more is the desire to ecologize these areas and, at the same time, to valorize the material contained in them, becoming the framework of these concerns which also fits the theme of this research.

The main objective is to develop efficient and economically viable physical and hydrometallurgical processing techniques in order to recover valuable metals and minerals from the slurry from the pond of the former chemical plant BICAPA Tarnaveni.

Aim of the work

- Slag preparation - examples of technological processes for processing/valorization of green sludge from the former Târnăveni factory pond;
- Their hydrometallurgical processing to recover the elements of interest
metals with potential for recovery.

Depending on the composition of the pond sludge and the useful minerals recovered from it, it can be used in different fields of activity.

This paper proposes solutions for the recovery of useful minerals from the Târnăveni chemical waste dumps, which could be part of the circular economy.

Recovery economy: focuses on the recovery of all resources, including waste. Exploitation of historical waste, which contains useful materials that can be reused to supplement the material requirements of a circular economy life cycle. For example, in the case of the green slurry resulting from the manufacturing process of chromium salts, it could have been a circular economy if it could have been reintroduced into the technological process through recycling. The closure of the company that generated this waste excludes from the outset the application of the circular economy concept to this case. However, the processing of this waste can contribute to covering the material needs of other material circuits. For example, in the case of magnesium, following the recycling of this metal by smelting with a eutectic mixture of sodium and potassium chloride, there is an imminent loss of metal in the smelter from which the recovered magnesium is separated, which must be replenished from external resources in a system specific to the circular economy.

Waste from the Târnăveni ponds, also known as green sludge, fits easily into the recovery economy. Turning this waste into a resource means a domestic consumption of raw materials, concentrated ores, oxides, raw or processed metals. This sllag becomes an important waste for final treatment and then disposal. Thus, metals such as aluminum, iron and nickel can be recovered from green sllag using different technological processes, consuming less energy than primary production, and without carbon emissions. For example, recycled aluminum production consumes 97% less CO_2 than primary production.

Another example of recovery from green slimes is the recovery of magnesium. The chemical composition of the green sludge is close to that of a semicarbonatized dolomite (burned at about 700°C), but there are two main differences:

- sludge contains much higher percentages of MgO, SiO_2 , Cr $O_{23;}$

- The MgO contained in the sludge is recrystallized in periclase which gives it a low chemical activity,

The technological solution presents the development of an integrated industrial platform for the resumption of the production of 99% pure magnesium, corm oxide, aluminum and iron by implementing sustainable technologies, without negative environmental impact, which will create value chains specific to the circular economy for the production of useful elements and materials. The implementation of circular economy principles focuses in particular on its own production process and for sustainable development in harmony with the environment.

CHAPTER 1. Technologies for the processing of chromium ores that generate green slimes

The technological process for the production of sodium dichromate at BICAPA Târnăveni was based on the reaction between chromium ore, dolomite and soda ash calcined at 1100-1250°C in furnace-type reactors with a length of 55 m and a diameter of 2.7 m protected inside with refractory brick.

After dosing of raw materials and oxidative roasting, wet grinding of the sinter in the furnace, settling and filtration took place. [58]

The filtration phase resulted in the so-called "green sludge", which was deposited in bins 2 and 3 and represents 80-90% of the hexavalent Cr content. [58] After evaporation (for concentration) of the chromate solutions by acidification with concentrated H_2 SO_4 , the change from chromate to dichromate took place and separation by centrifugation of the sodium sulfate further processed as by-product. [19]

Sodium dichromate plants by their very nature generated toxic waste. Toxicity was given by the presence of Cr^{6+} . All the waste resulting from the filtration phase, the so-called "green sludge" as well as that resulting from cleaning, deposition on the machines (crust, dust, decanted suspensions, etc.) was deposited with great strictness only on bins 2 and 3. [58]

After concentration of the dichromate solutions in 2 steps with further separation of the sodium sulfate, crystallization of the dichromate solutions, centrifugation, drying and packaging of the sodium dichromate took place.

The chemical composition of the green sludge as well as of the sludge from the sewage treatment plants are given in the tables below (the samples were taken at random and mixed to obtain an average sample):

Table 1.1.Chemical composition of green sludge - chromate filtration batches 2 and 3 [%]

Component	Sample I	Test II
Cr O_{23} soluble in water	2,2	1,73
Cr O_{23} solubinHCl	2,8	3,01
Cr O_{23} total	9,6	11,65
SiO_2	9,8	5,92
$Al2O_3$	5,4	6,0
$Fe2O_3$	8,38	8,38
MgO	28,9	24,85
CaO	26,0	24,39
P.C	8,12	10,81
H2O	40,2	-

Table 1.2. Chemical composition of sludge - treatment plant

Component	Value [%]

$Cr_{2\ \text{Total}\ O3}$	7,09
Cr_{total}	4,85
Cr^{3+}	1,3
Cr^{6+}	3,55
CaO	14,58
MgO	3,18
Faith O_{23}	7,66
Insoluble in HCl	10,22
SO_4^{2-}	14,35
P.C.	40.11(1000° C)

CHAPTER 2. Theoretical considerations on green sludge valorization processes

2.1. Green sludge exploitation procedures

An exploitation depends primarily on the configuration of the land and the position of access roads. Depending on these factors, top operations are created in the case of terraces and deep operations in the case of deserted beds. The aim is always to make use of all the advantages offered by the terrain in order to organize gravity transport as far as possible and, above all, to avoid unnecessary transport, ensuring that the operation is in continuous and constant operation without interruption. When a terrace is being exploited, the first operations will consist in clearing and laying out the coastline in order to create a working face and platform. [19]

The Târnăveni battals can be exploited by ballast technologies, as the access roads are in the immediate vicinity, and the platform for preparing the exploited elements is also built next to them, so it does not require additional transportation or hoeing costs.

The chapter analyzes various theoretical methods of green sludge recovery, including both physical and chemical separation methods:

- Hydrocyclone separation: This method uses centrifugal force to separate larger or heavier particles from finer or lighter ones, giving higher classification accuracy than other methods.
- Oscillating Table Concentration: The process uses water currents and table oscillations to separate mineral particles according to specific gravity, and is useful for ores less than 2-3 mm in size.
- Magnetic separation: The method is based on differences in the magnetic properties of minerals, using magnetic fields to deflect magnetic particles from their paths.
- Electrical separation and ultracentrifugation: These techniques rely on differences in conductivity and centrifugal force to separate particles from the slurry.

Chemical separation methods are also discussed:

- Leaching: The process involves the dissolution and extraction of metals from the slurry and is influenced by factors such as temperature, pH and concentration of reactants.
- Magnesium oxide precipitation: Factors influencing solubility and precipitate formation are explored, providing a theoretical basis for optimizing separation processes.

CHAPTER 3 Description of the green sludge ponds belonging to the former S.C. Bicapa S.A. Târnăveni

This waste looks like ordinary 'ballast', but it contains hexavalent chromium - a carcinogen - in addition to other heavy metals. Over time, these residues have been deposited, and today they look like hills of sterile waste. It has been estimated that there are about 2.5 million tons of waste material here

The baths contain, as a result of the activity in the production of chromium compounds (sodium dichromate, potassium dichromate, chromium trioxide), sulphur-based anti-radicals, barium salts, fluorine products, aluminum sulphate, zinc oxide and tiles.

The green slurry bins on the BICAPA platform are more than 25 years old since they were last used for waste storage. At present, due to the occurrence of cementation phenomena of the deposited material, at the same time as the material is drying out, the surface of the piles is compacted, the material being very difficult to exploit even with an excavator (during the digging of some test trenches, the machine is lifted with the front of the tracks in the air). Once excavated, the material was found to be wet, plastic with a clayey appearance at depth.

In order to know the exact state of the material deposited in the battals, 72 boreholes were drilled, with sampling from meter to meter. In this way, 862 samples were extracted, of which 847 were also analyzed for density.

The characteristics of the battles are:

- Total area 145931 m^2 .
- Perimeter 1512 m
- H med 12 m
- 30° slope inclination
- Ground projection 13.85 m
- S talus 20941 m^2 (ground projection)
- The maximum annual precipitation discharge over the entire catchment is 100400 m^3 .
- Maximum annual flow of water from precipitation on the slope 14408 m^3

The following situations have been encountered in the determination of the density of pond samples

- Cores with a density less than 1 kg/dm^3 - which is due to the existence of suffocation and drainage phenomena, as a result of which air voids have appeared in the mass of the deposit. Suffusion in this case is the phenomenon of entrainment of the finest particles by the seepage water, also processes of dissolution of soluble chromate salts or processes of dissolution of magnesium carbonate by carbon dioxide in the seepage water.
- Carrots with a density of 1 - 1.4 kg/dm^3 for which there are two situations:
    - For the surface material this low density is due to the very high porosity of the dry material;
    - In the case of depth material this density is explained by the existence of liquid suspension lenses.
- Carrots with a density of 1.4 - 2.1 kg/dm^3 characteristic of green slime with a normal moisture content of 15 - 30%;

- Cores with a density of > 2.1 kg/dm^3 due to the presence of rocks, construction waste, cleaning waste and ore (chromite).

The distribution of the concentration of the useful elements in the volume of the batches is essential for determining the mining technology. For a continuous technological flow it is very important that the process feed material should be as constant in composition as possible.

The results of the chemical analysis of the 862 samples show that the concentration of the useful elements Mg and Cr is relatively constant in the volume of the two batches. Due to this fact, it is not necessary to selectively exploit the material in order to ensure a material with constant characteristics in the plant feed.

In conclusion, the exploitation of green slurry in the battals does not have to be selective, but due to the presence of air or liquid slurry pockets it is not recommended to station heavy machinery on the surface of the green slurry, nor to use trenching methods of exploitation in which the heavy machinery circulates. For this reason, machinery and mining methods should be chosen which do not involve the presence of any equipment on the surface of the battals.

In addition, due to the very easy leaching of the chromate ion, for environmental protection reasons, the hydraulic exploitation of the slurry is excluded.

CHAPTER 4. Preliminary green sludge valorization tests

The wet granulometric wet analysis shows that the fine fraction is found in a high proportion in the material about 58 % being less than 0.04 mm, in this class being found calcium above the average of the other classes, the higher proportion of other useful elements is located in the coarse classes.

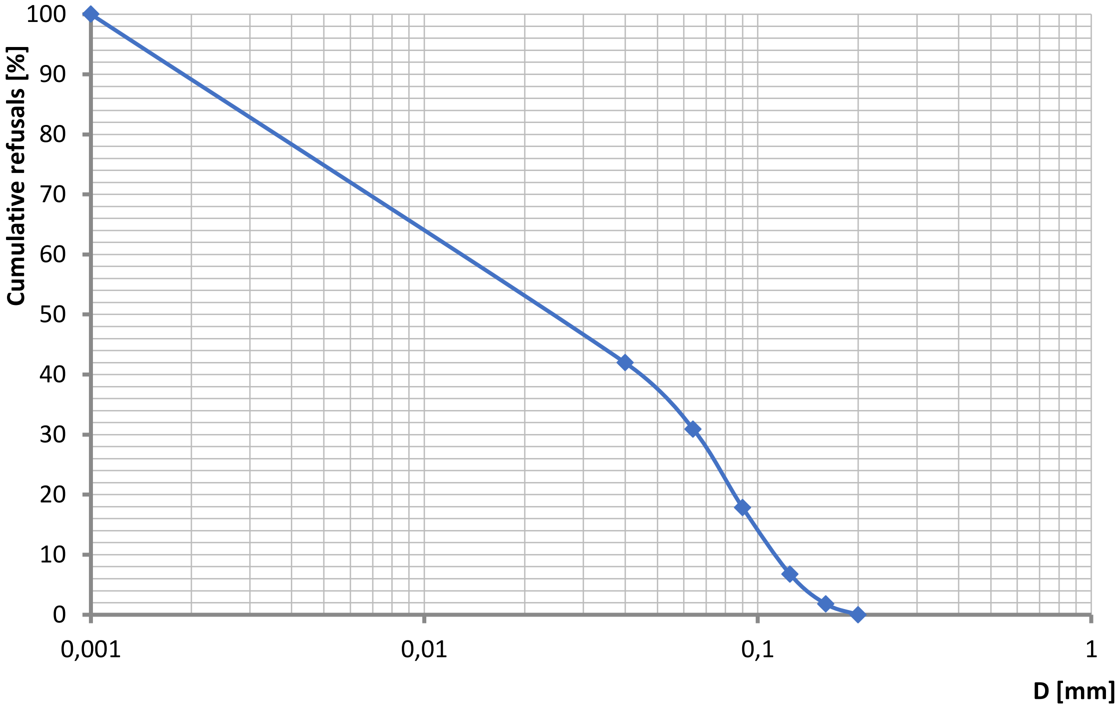

Figure 4.2. Granulometry of materials

Source retrieved: S.C. Wastes Ecotech S.R.L. (INCDMRR study)

In order to separate the useful elements from the green slurries, separation tests were initially carried out by more economically advantageous physical separation methods: particle size separation, magnetic separation, electric field separation, hydrocycloning separation, ultracentrifugation separation, vibrating table separation and flotation.

The physico-mechanical processes checked did not allow the separation of the constitutive elements, not even their satisfactory preconcentration, whether they were called gravitational processes allowing separation based on the density difference between the components, or flotation based on the surface properties of the particles, or electrical separation.

Even at a fine grain size, specific minerals of the component elements cannot be identified and separated.

A more advanced grinding, in addition to a high energy consumption, causes micronization of the particles, their separation not being possible by the above-mentioned processes.

The only process that allowed to obtain favorable results was the magnetic separation in weak field to obtain a marketable iron concentrate but its extraction by weight is somewhere below 5%. This process at this stage does not allow the complete removal of iron from the sample

Further research has shown that applying the process after heat treatment of the sample material in a chemical treatment step would improve iron recovery.

From what has been analyzed, it can be seen that the component elements are intimately linked to each other without constituting mineral-specific structures. For this reason separation by mechanical processes are neither efficient nor advantageous for the extraction of useful minerals from the Târnăveni slurries.

CHAPTER 5. Exploitation of green shale from slurries

For the exploitation of the material in the ponds, the gravel mining method was proposed.

The gravel digger is a variant of the dragline, where a different type of bucket is used, the arm and other attachments of the excavator remain the same. The gra grapple bucket can be of different types according to the capacity and the number and shape of the jaws.

The cup is supported by a support cable, which is used to raise and lower it. The closing and opening of the cup is done with a second cable, called the maneuvering cable. [19]

For the exploitation of the pond material, the technological flow of module 1 was proposed.

Module 1. It is realized by hydraulic extraction and transportation of the material. This module can be located in the immediate vicinity of the green slurry battal and is intended to form a hydraulic slurry-water mixture, which ensures a constant and controlled flow rate to the plant. The proposed feed rate for an operating life of 8 years is 30 t/h of dry material, which corresponds to 39 t/h of material mined from the pile.

CHAPTER 6. Stage I recovery - recovery of chromium, magnesium and calcium

Module 2. Material conditioning. This operation is essential for the smooth running of subsequent technological processes as it increases the reaction surface of the material particles.

In this module there is the attrition of the material particles followed by a control classification, with shredding of the super granulation.

Module 3. Material washing. In this module a partial removal of hexavalent chromium takes place. This module can be waived if two-step magnesium extraction is chosen.

The chemical reactions that take place in this module are:

$$CaCrO4 + Na_2\ CO_3 = Na_2\ CrO_4 + CaCO_3$$

The role of this reaction is to increase the solubility of the chromate ion and insolubilize the calcium ion.

$$MgCrO_4 + Na_2\ CO_3 = Na_2\ CrO_4 + MgCO_3$$

The role of this reaction is to insolubilize the magnesium ion.

Module 4. Magnesium extraction. In this module magnesium extraction by carbon dioxide leaching takes place.

The material from the pre-stage, module 3, is leached with CO_2

The chemical reactions that take place are:

- in the flotation machine:

$$MgCO_3 + CO_2 + H_2\ O = Mg(HCO\ )_{32}$$

- in the kettle:

$$Mg(HCO\ )_{32} = MgCO_3 + CO_2 + H\ O_2$$

We note that the chemistry of these processes is much more complex, and the two reactions are described in a simplified way.

The use of flotation machines is recommended for magnesium leaching because their aerated agitation system ensures intimate contact between the solid particles and the leaching solution.

The resulting solution contains magnesium dicarbonate and chromate ion. Separation of the chromate ion can be achieved by ion exchange. Anions such as AMBERLITE PWA7 or AMBERLYST A21, usable in the neutral pH range, are recommended as ion exchange mass. AMBER SEP 4400 HCO_3 used in sodium carbonate medium for uranium extraction.

Module 5. Purification of magnesium carbonate. The realization of this module is optional, it will be introduced in the final technological flow, but only if it is chosen to obtain a high purity magnesium oxide.

Both in construction and in principle, this module is identical to module 4. For this reason, it is possible to opt to produce the magnesium carbonate in module 4 in stock, and to shut down the plant periodically in order to switch to mode 4 in order to purify the magnesium carbonate produced in stock.

Module 6. Calcium extraction. The role of this module is to remove calcium compounds from the residual slurry resulting from modules 4 and 5. Calcium removal is very important because it retains hexavalent chromium and keeps the waste in the hazardous waste category. Tests on the original material have shown that the extraction of calcium by this process, without activation by calcination, is very low (3.3%). Therefore, activation of calcium by calcination at 850° C. The chemical reactions that take place are:

- calcium activation: $CaCO_3 = CaO + CO_2$
- calcium extraction: $CaO + 2NH_4\ Cl = CaCl_2 + 2NH_3 + H\ O_2$
- recover NH_4 Cl: $NH_3 + NaCl + CO_2 + H_2\ O = NH_4\ Cl + NaHCO_3$

- production of sodium carbonate: $NaHCO_3 = Na_2\ CO_3 + CO_2$

Module 7. Purification of calcium chloride solution. In this module, the hexavalent chromium is removed and the magnesium not extracted in module 4 is recovered.

The chemical reactions that take place are:

- chromate ion removal ion exchange
- remove magnesium: $MgCl_2 + NH_4\ H2PO_4 = MgNH_4\ PO_4 + 2HCl$
- neutralizing CaCl solution$_2$: $2HCl + Ca(OH)_2 = CaCl_2 + 2H\ O_2$

Stage II recovery , disposal of the final residue from Stage I recovery

The technological process step, ***Module 8,*** is iron recovery. The role of this module is to extract the sulphuric acid soluble iron from the ferrous slurry. It should be noted that this iron, which is found in the form of a very fine powder, still maintains the cohesive character of the sludge. It is only after its removal that the mineral particles in the slurry are completely liberated and can be separated by physical, gravitational processes. The chemical reactions that take place are:

- iron leaching: $FeO + H_2\ SO_4 + 6H_2\ O = FeSO_4 \times 7H\ O_2$

- recover sulphuric acid: $FeSO_4 \times 7H_2\ O = Fe\ O_{23} + H_2\ SO_4 + SO_2 + H\ O_2$

Module 9. Final residue separation. The role of module 9 is to separate the different types of minerals in the residue remaining after iron extraction in module 8. These are separated by physical methods only. No chemical reactions take place in this module. Mainly the separation of unreacted chromium ore takes place in this module.

Rare metal recovery is carried out in ***Module 10.*** Rare metal recovery takes place at this stage. Their recovery can be achieved by leaching with sodium hypochlorite or more efficiently with a mixture of hydrochloric acid and nitric acid. The reactions that occur when using a mixture of hydrochloric acid and nitric acid are described below. It should be noted that good results have also been obtained experimentally using sodium hypochlorite. The final technology will be selected during pilot tests when a larger amount of residue will be available. The chemical reactions taking place in this module are:

- rare metal oxidation: $3Ir + 18HCl + 4HNO_3 = 3H_2\ IrCl_6 + 4NO + 8H\ O_2$

- iridium cementation: $Na_2\ IrCl_6 + 2Zn = Ir + 2ZnCl_2 + 2NaCl$

- precipitation rhenium:$2NaReO_4 + Zn(NH\ )_{34}\ Cl_2 = Zn(NH\ )_{34}\ (ReO\ )_{42} + 2NaCl$

Module 11. Sodium chromate crystallization. The purpose of this module is to extract sodium chromate from the wash water. No chemical reactions take place in this module, only evaporation-crystallization processes.

The role of this module is to purify the wastewater resulting from the process of neutralization of the green sludge and to extract the useful elements remaining in it.

Additional or alternative technologies for green sludge recovery

From a technological point of view, the purification of carbonate solutions by ion exchange has proved to be cumbersome because of the danger of precipitating $Mg(OH)_2$ in the ion exchange mass, clogging it. For this reason, it was necessary to consider other methods of hexavalent chromium separation, such as electrodialysis, which would cause the chromate ions to migrate out of the carbonation solution.

To test the process for the extraction of chromate ion from carbonate solutions, we used a three-compartment electrodialysis cell of our own construction. Within the electrodialysis cell the membranes were placed between the three chambers, a central chamber into which the crude carbonate solution is introduced, laterally flanked by an anionic chamber in which hexavalent chromium is concentrated as chromic acid and a cationic chamber in which magnesium ion associated with the chromate ion is concentrated as magnesium hydroxide (Figure. 6.9). Filter paper was used as the separating membrane.

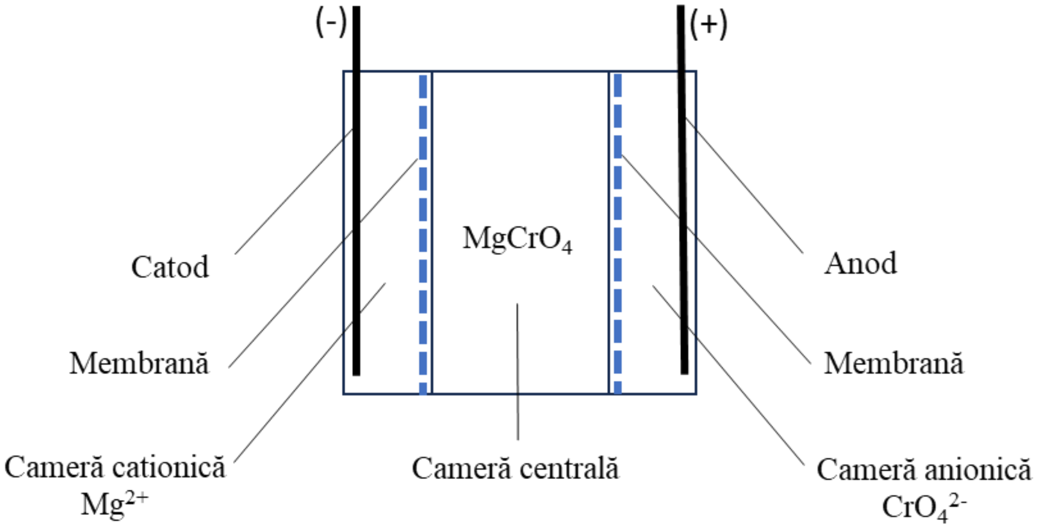

Figure 6.9. Schematic of the electrodialysis cell

The chromate ion in the carbonation solution is found as magnesium chromate, which is easily soluble. In the electric field of the electrodialysis cell, the dissociation of the chromate ions from the magnesium ions takes place, transporting them to the side compartments: the chromate ion to the anionic compartment, where it accumulates as chromic acid (H_2CrO_4) and the magnesium ion to the cationic compartment, where it accumulates as magnesium hydroxide ($Mg(OH)_2$).

CHAPTER 7. Techno-economic efficiency of the proposed process for the exploitation of green shale

In order to analyze the techno-economic efficiency of the proposed process, mass and energy balances had to be carried out.

The PhD thesis presents in detail the mass balance realized after the tests carried out in the pilot station of Târnăveni for the first stage of processing and in the laboratory of the University of Petrosani for the second stage of processing.

The figures and table below summarize the mass balance conclusions:

Figure 7.6 shows the evolution of the green slurry mass during all technological tests for a 10 kg quantity:

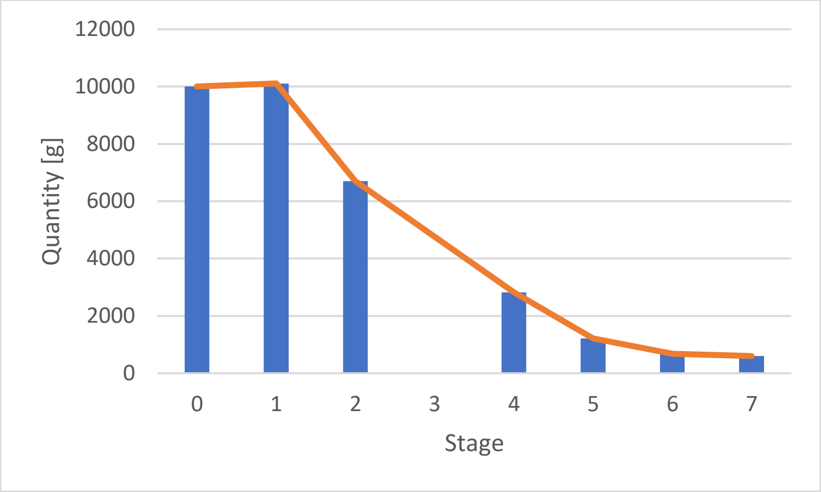

Figure 7.6. Evolution of green slurry mass during the technological tests

From the above figure it can be concluded that by applying the green sludge recovery technology, 94% of the original mass is removed from the waste

Figures 7.7. to 7.11. show the recovery of useful elements during all the technological tests for a 10 kg quantity.

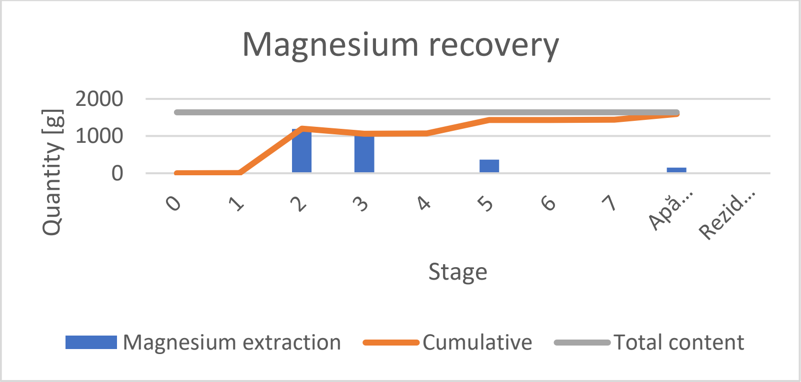

Figure 7.7. Magnesium recovery for technological process steps

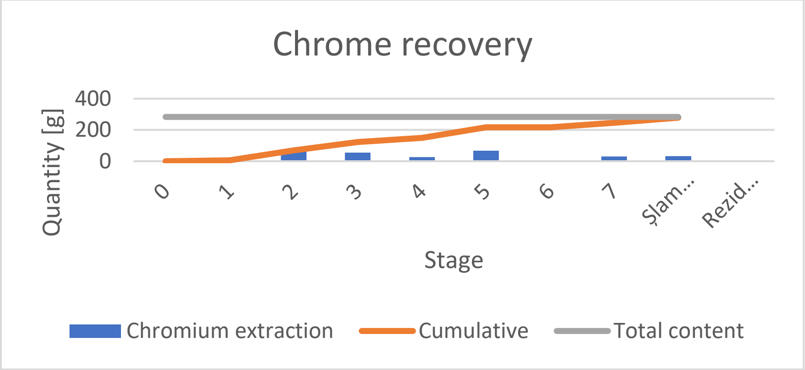

Figure 7.8. Chromium recovery for technological process steps

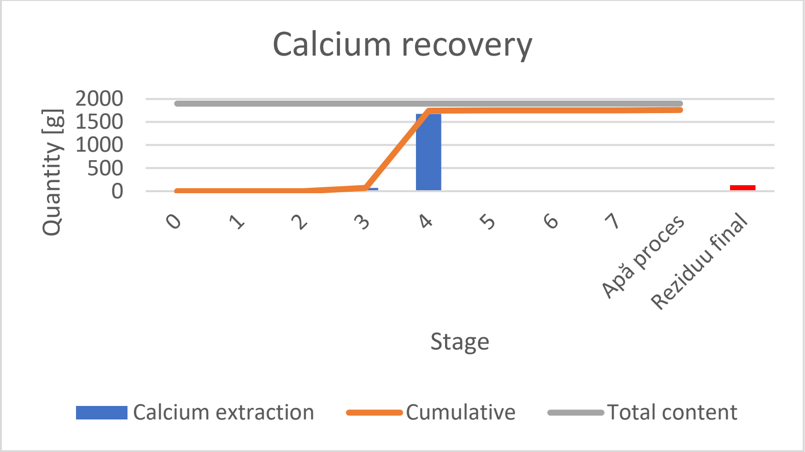

Figure 7.9. Calcium recovery for technological process steps

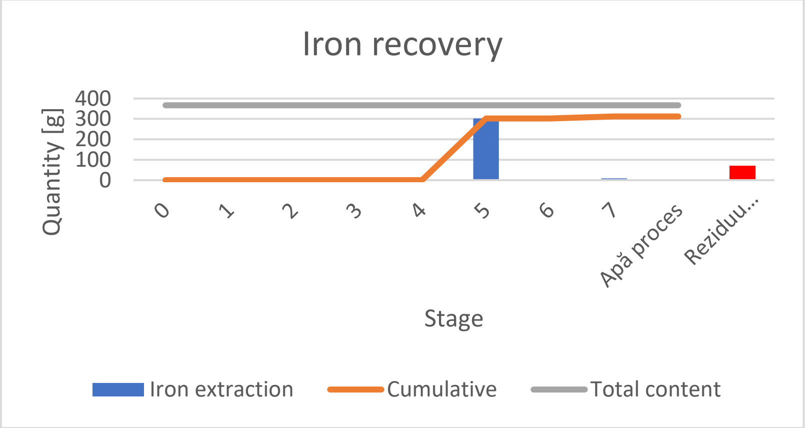

Figure 7.10. Iron recovery for technological process steps

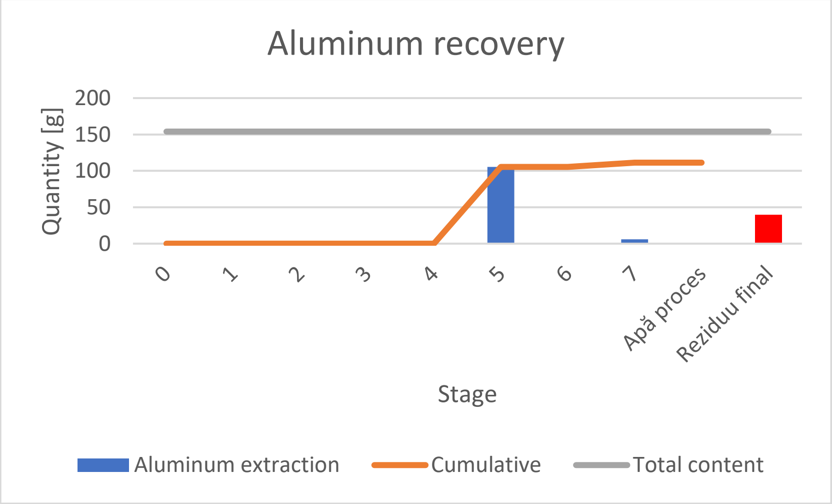

Figure 7.11. Aluminum recovery for technological process steps

As a final conclusion, Table 7.3. shows the recovery of the main useful elements contained in green shale:

Table 7.3. Recovery of the main useful elements contained in green shale

Item	UM	Retrieve
Mg	%	97,23
Cr	%	98,20
Ca	%	92,71

Faith	%	85,08
At	%	72,26

The following observations were also made during testing:

1) Upon leaching with NH_4 Cl it was observed that nickel is extracted from the material. An additional test was carried out to recover this element by precipitation with dimethylglyoxime. Recovery was complete due to the insolubility of nickel dimethylglyoxime, but this separation was not included in the balance;

2) On sulfidation, after separation of iron, aluminum and crystallization of aluminum sulfate, rhenium was found to be present in the mum solution. Rhenium was extracted by precipitation as diamino zinc perreninate with diamino zinc chloride, but this separation was also not included in the balance

3) Chemical analysis of the technological samples showed the presence of vanadium and strontium, but these elements were not extracted.

In the case of the energy balance for the technological process proposed for the industrial plant, taking into account all machinery and operations, for a processing capacity of 30 t/h green (dry) slurry, the energy consumption results as follows:

Table 7.4. Energy balance.

Module	gas	electricity	Diesel
	MWh	kWh	l
Module 1. Hydraulic material extraction and transportation		69,0	87,2
Module 2. Material conditioning		93,8	
Module 3. Material washing		598,6	
Module 4. Magnesium extraction	2,5	595,4	
Module 5. Purification of magnesium carbonate	2,5	388,2	
Module 6. Calcium extraction	20,1	919,9	
Module 7. Purification of calcium chloride solution		141,8	
Module 8. Iron recovery	1,6	150,5	
Module 9. Final residue separation		80,9	
Module 11. Sodium chromate crystallization.	7,2	46,9	
Module 12. Wastewater treatment	1,4	106,8	
Total	35,4	3191,6	87,2

Note: Module 10 - Separation of noble matals has been excluded from this balance sheet.

The share of energy consumption per module in total energy consumption is shown in Figure 7.12.

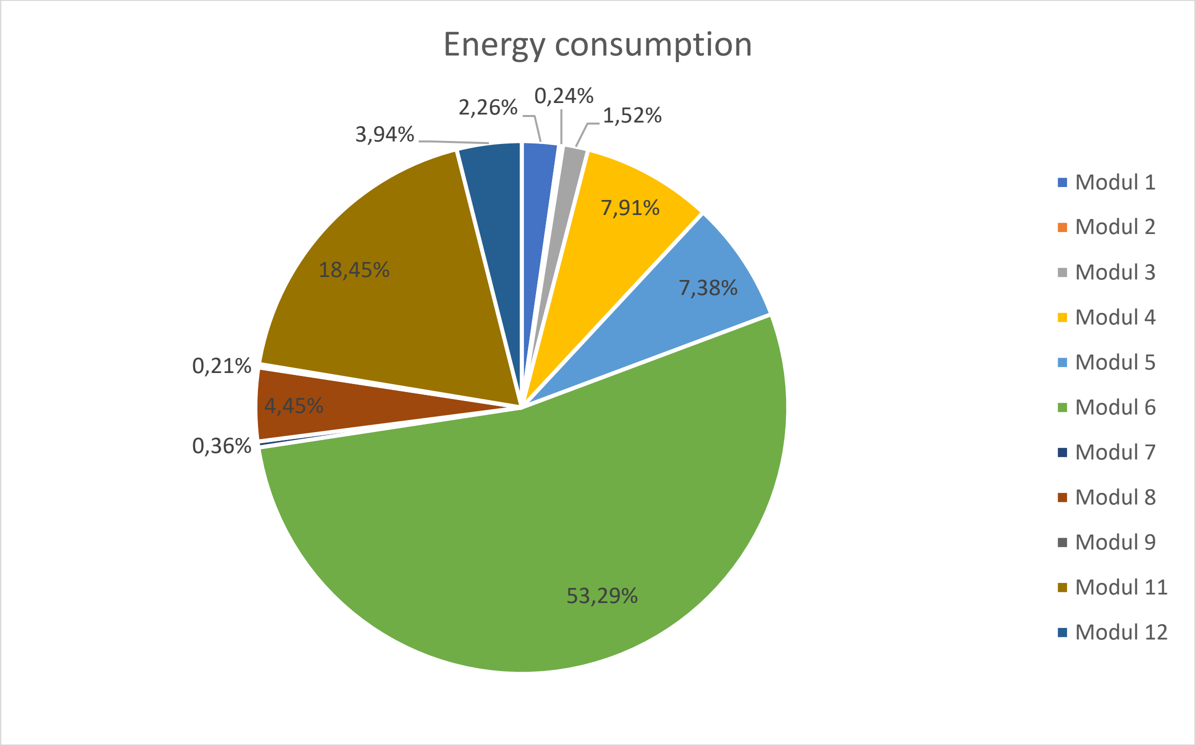

Figure 7.12. Share of module energy consumption in total energy consumption.

The diagram shows that Module 6 - Calcium extraction accounts for 53.29% of the total energy consumption. This module is not important for calcium extraction but for the fact that it releases the calcium bound chromate ion as $CaCrO_4$, which is hardly soluble.

Table 7.7 gives an estimate of the profit resulting from the operation of the plant.

Table 7.7. Estimation of the profit of the green shale recovery plant

Specification	RON	EUR
Total investment	103.122.310	22.773.859
Total construction	12.538.531	2.769.049
Hourly operating costs	20.110	4.441
Monthly salary expenditure	178.909	39.511
Production goods hourly	175.704	38.803

Annual investment amortization	14.457.605	3.192.863
Annual operating costs	178.313.414	39.379.301
Specific operational costs (per tonne)	468	103
Annual commodity production	1.539.164.570	339.913.997
Profit	1.346.393.551	297.341.832

Table 7.7. shows that the profit margin of the proposed invention is very high, primarily due to the production of high purity and high value products.

CONCLUSIONS AND PERSONAL CONTRIBUTIONS

CONCLUSIONS

In Romania, hexavalent chromium was manufactured at the Târnăveni Chemical Combine in a process that produced a hazardous waste called green sludge, which was stored in two batalys, in a quantity of about 1 million tons. Fortunately, the ponds were built according to certain rules which avoided contamination of surface and groundwater.

Sodium chromate is manufactured by oxidative roasting of chromium ore with sodium carbonate in the presence of dolomite as mordant. The use of dolomite has led to the formation of green sludge, consisting of ore tailings, ore slag and calcium and magnesium chromates.

In Romania there have been attempts to recover this waste, both at the Târnăveni Chemical Combine and at the Traian Vuia Polytechnic Institute in Timișoara. Most of these attempts were aimed only at recovering useful elements without considering the disposal of this waste. In the latter, there have only been attempts to use it in the manufacture of Marbel glass, and some cement sorts, but without notable results in this case.

Recovery tests of hexavalent chromium by water washing under different conditions have been carried out with results considered satisfactory at the time but totally unacceptable today.

Tests were also carried out to extract the magnesium from the waste, but it contained more than 1% calcium oxide, which severely limits its price on the market.

The tests on the use of green sludge in the manufacture of glass had satisfactory results, only qualitatively, because all the characteristics of the finished product were only calculated, none of them being determined by measurements.

The pilor-phase carbonation tests were performed in the Na$_2$ CO /NaHCO$_{33}$ system, which I consider irrelevant for green shale, where a three-phase system is involved.

Tests for the design of a pressurized reaction vessel have also been carried out on the model, but these have only considered the design of agitation and not other essential parameters such as the dispersion of carbon dioxide in the reaction medium.

Similar concerns have not been identified worldwide, with most references addressing a similar process for extracting magnesium from dolomite, of course in the absence of hexavalent chromium.

Carbon dioxide leaching has proven to be very effective and selective when applied in two or step leaching.

Separation of hexavalent chromium with sodium carbonate from the green sliver is effective but results in a solution heavily polluted with calcium and magnesium ions.

The processing of the residual sludge is necessary in the further waste disposal process as it still presents hazardous waste characteristics.

The green sludge deposited in the former chemical plant BICAPA S.A. Târnăveni constitutes a permanent danger for the environment due to the toxicity and high mobility of the chromate ion. Hexavalent chromium is one of the most restricted heavy metals in water and soil after mercury, thallium, cadmium, beryllium and selenium;

The sludge deposited in ponds is an important resource of magnesium and chromium, for the valorization of which research began in 1978. The material deposited in ponds has high variations in density, air voids and pockets of liquid slurry, which make it unsuitable for mining with heavy-duty equipment;

Due to the high mobility of the chromate ion, hydraulic extraction of the green slurry from the pond is ruled out, even though this process was initially considered to be favored;

The best solution for extracting green sludge from ponds is to use long-arm gravel pits on the pond embankments;

A new technology, unidentified for other similar resources in the world, has been developed for the utilization of green shale, which is a combination of existing technologies.

After extraction from ponds, the material must be activated by wetting and attrition in order to achieve the best possible dispersion in the water;

Magnesium is extracted by carbonation, following the Pattinson process. Industrially, two countercurrent carbonation steps are necessary to obtain the highest extraction yield. Carbonation is proposed to be carried out in flotation machines, at a speed and stator-rotor distance setting chosen so as to cause the gas bubbles to collapse. Magnesium carbonate was purified by recarbonization to obtain a product of the highest possible quality.

Calcium is extracted by adapting the Solvay process for the manufacture of sodium carbonate to obtain calcium chloride (which is a waste product in soda ash manufacture). Without this step, the removal of hexavalent chromium is impossible because of the low solubility of calcium chromate. The option of removal in the form of calcium chloride was chosen because this product is widely used as a road de-icer instead of sodium chloride.

The chromate ion is extracted and the process water is extracted by ion exchange, using resins specific to the extraction of the chemically similar uranyl ion;

The sludge remaining after the extraction of the calcium is still hazardous waste, which does not meet the legal conditions for landfilling in hazardous waste landfills, obliging the project holder to process it further;

The hexavalent chromium remaining in the slurry resulting from calcium extraction is bound by adsorption to hydrated iron and aluminum oxides and silicate gels. In order to mobilize the chromate ion, the iron and aluminium, together with the magnesium refractory to carbon dioxide extraction, are solubilized with sulphuric acid and the silica by leaching with sodium hydroxide.

The residual chromium in the final waste can be extracted very easily by separation on vibrating tables.

For the pilot phase, the technological flow was divided into two stages. The first stage consists in the extraction of magnesium, chromium and calcium and was carried out in the pilot plant on the industrial platform of the former BICAPA S.A. Târnăveni. The second stage, processing the final waste, was carried out in the chemistry laboratory of the University of Petrosani.

The mass balance was also drawn up separately for the two stages;

1. For the mass balance all volumes of liquid effluents were measured, their density was determined and all solid effluents and gaseous influents (CO_2) were weighed;
2. In contrast to the proposed industrial process, no liquid and gaseous effluents were recirculated in the pilot plant; 64 solid and liquid samples were also taken and analyzed in the laboratories of the University of Petrosani.
3. Pilot tests and mass balance allowed the extraction yields of the main useful elements to be calculated:

Item	UM	Recovery [%]
Mg	%	97,23

Cr	%	98,20
Ca	%	92,71
Faith	%	85,08
At	%	72,26

The final residue resulting from the extraction of the useful elements proves to be a non-hazardous waste, in the proportion of 10%.

PERSONAL CONTRIBUTIONS

- We proposed and implemented the magnesium extraction process by carbon dioxide leaching for the processing of green slimes, in contradiction with foreign consultants who recommended hydrochloric acid leaching, also widely used for extracting magnesium oxide from dolomite.
- We have adapted the process of extracting magnesium by leaching with CO_2 in pressurized autoclaves using flotation machines, at a speed and stator-rotor distance setting chosen so as to cause the gas bubbles to collapse;
- We have proposed and implemented the leaching of magnesium carbonate in two or three steps in order to remove calcium from the product and thus purify the final product.
- We have adapted the Solvay sodium carbonate process for the extraction of calcium as calcium chloride;
- We have proposed the separation of hexavalent chromium with sodium carbonate, as sodium chromate, a form in which it is highly soluble. We carried out tests for the separation of chromium from carbonate solutions by electrodialysis
- We identified the optimal anionic anion exchangers for the extraction of chromate ion from alkaline solutions;
- We proposed the use of a sulfuric acid final residue leaching process, used in titanium metallurgy and which is provided in the BREF as a BAT process, for iron and aluminum extraction.
- We proposed a process for the recovery of noble metals from the final residue by sodium hypochlorite leaching.
- We have identified the presence of nickel, vanadium and rhenium in the material and have developed and tested technologies for the recovery of nickel and rhenium, and have identified a suitable technology for the recovery of vanadium.

FUTURE DIRECTIONS

- To identify an effective process for removing calcium before treating the final residue from carbon dioxide leaching, so that this element no longer disturbs the sulphuric acid leaching process, in contact with which it produces calcium sulphate, which is hardly soluble and has a pronounced tendency to harden.
- To identify a technology for the recovery of hexavalent chromium from the solutions resulting from the carbonation of green shale, since extraction with sodium carbonate proved to be too difficult and also inefficient, due to the presence of soluble calcium in the system, with which the chromate ion forms a hardly soluble compound. With this in mind, we started research on chromium extraction by electrodialysis.
- Identification of technological solutions for the most advanced recovery of other components of the green sludge in order to minimize the final residue volume.
- Developing processes to recover rare metals extracted by leaching as impurities.
- Deepening nickel and rhenium recovery technologies and identifying ways to extract vanadium and strontium.

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