Pyroprocess Experiments at ENEA Laboratories

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1. Introduction

Pyrochemistry is a term referred to process reactions at high temperatures. At present it appears as a promising alternative for the separation of actinides fission products from lanthanides, which is ordinarily carried out in eutectic molten chloride salts, such as LiCl-KCl. This method is expected to be very suitable for advanced nuclear engineering due to its many advantages compared with the hydrometallurgy process currently used for the extraction of lanthanides from metal fuel. They include: radiation stability of molten salts (allowing processing of spent fuels of high radioactivity); absence of neutron moderator such as water; low waste production; non-proliferation requirements.

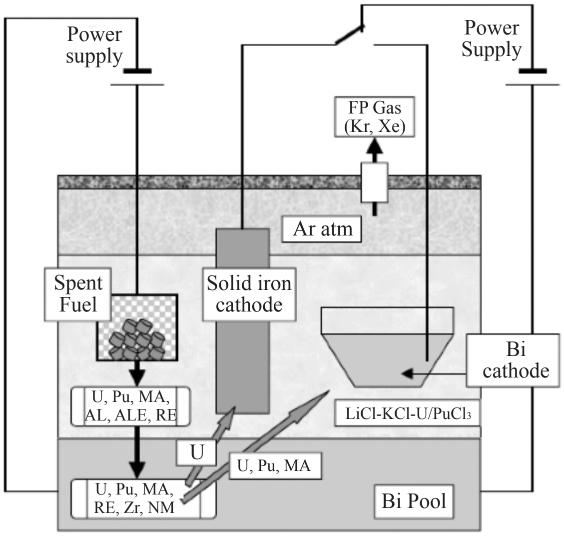
Since many years ENEA is involved in research programmes concerning separation of actinides from lanthanides and treatment of related wastes. The facilities recently installed for carrying out experiments in this field are described herein, together with data related to some experiments.

2. Pyrel III Electrolyzer for Process Studies

Electrorefining is the key step in the pyroprocess for recovery of actinides (uranium and transuranic elements) by using electrochemical difference among elements in molten LiCl-KCl salt and liquid bismuth under high-purity argon atmosphere at 773 K [1,2]. Chopped spent fuel segments are placed in a perforated steel anode basket and lowered into the electrolyte salt. Noble metals are collected by the liquid bismuth in metal form, while the other elements are dissolved into the salt in the form of their chlorides.

Actinides are recovered at two different cathodes: a solid steel cathode, at which almost pure uranium is collected; a liquid-bismuth cathode, at which plutonium chloride is reduced and collected with uranium, other transuranic elements, and a small amount of rare-earth fission products. Chemically more active elements (alkali-metal, alkaline-earth, and rare-earth elements) remain in the salt (Figure 1).

A pilot plant termed Pyrel (Pyrometallurgical electrorefiner) III has been installed at ENEA laboratories for pyrochemical process studies under inactive conditions (Figure 2) [3]. This plant is an improvement with respect to previous Pyrel II [4]. The crucible of Pyrel III consists of a zirconia container (125 mm ID x 130 mm high), inserted in a steel vessel (Figure 3) externally heated by a furnace (Figure 4) supported in an externally water-cooled well under the floor of a steel glove-box (about 0.95 m wide, 0.55 m deep x 0.85 m high), where an argon atmosphere is



MA : Minor Actinides RE : Rare Earths NM : Noble Metals
AM : Alkaline Metals AEM : Alkaline Earth Metals

Fig. 1. Electrorefining step of pyrometallurgical process.

Fig. 2. General view of Pyrel III plant.

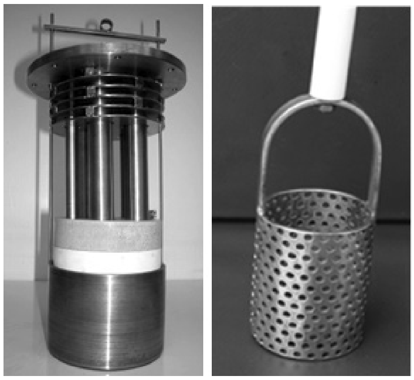


Fig. 3. Crucible of the plant *(left)* and anode basket *(right)*.

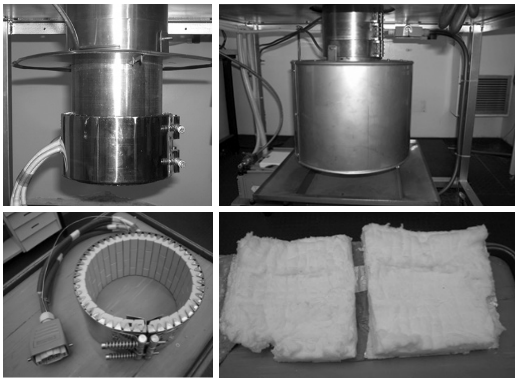


Fig. 4. External vessel, heating system, and thermal insulation.

Fig. 5. Steel cathodes of increasing diameter.

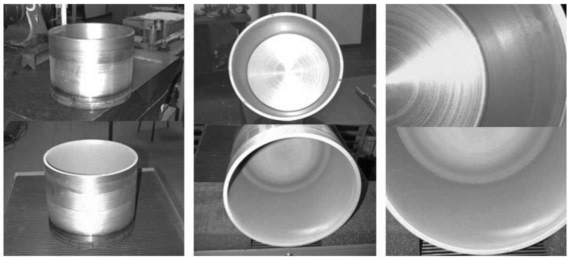


Fig. 6. Steel crucible before *(top)* and after *(bottom)* internal coating with alumina and silica by means of plasma spraying and plasma enhanced chemical vapour deposition.

maintained by a continual purge of about 10 L·min^{-1}. The crucible is loaded with 1.39 kg LiCl-KCl eutectic (59-41 mol%) and is currently operated at 460°C, in order to keep the vapour pressure of the salts down to acceptable values. Five perforated disks of a special steel are welded just below the main flange, in order to refrain the heat from reaching the floor of the glove-box (Figure 3). The height of the liquid salt inside the crucible reaches 7.0 cm. The insulated top plate of the electrorefiner has six slots for the stirrer, the thermocouple tube, two reference electrodes, the fuel dissolution basket, and the cathode.

The oxygen content of the glove-box atmosphere is maintained below 20 ppm, and the moisture below 10 ppm during all the operations.

The glove-box is fitted with over- and under- pressure tips. It is also equipped with a transfer box (38 cm long, 19 cm OD) to limit the oxygen entrance during posting.

The chromel-alumel thermocouples allow to record the temperatures corresponding to the salt bath, the gas zone immediately over the salts, the gas zone over the crucible, the internal and external floor of the glove-box, within ± 0.5°C during the experiments.

The electrodes are connected to an Amel Instruments galvanostat-potentiostat (Model 7050) with data logging via PC. The cell voltage is recorded together with the anode and cathode potentials during each experiment.

Steel basket anodes (Figure 3) and bar cathodes (Figure 5) are removed from the bath at the end of the experiments and analyzed. The cathode deposit normally contains up to 85-90wt% of salts, together with deposited metal.

The need for using a zirconia crucible comes from previous experiences with steel crucibles. In spite of the internal coating (Figure 6), made by applying an alumina

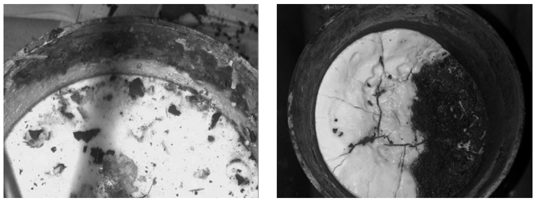


Fig. 7. Interior of a steel crucible at the end of an experimental campaign showing the salt layer *(left)*, and the bismuth layer *(right)* after the partial removal of the salt with hot water.

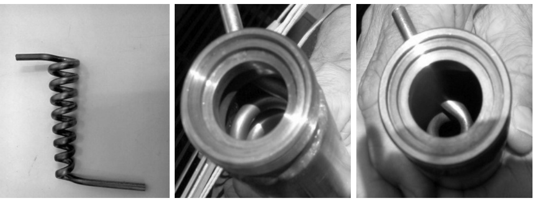


Fig. 10. Trap *(left)* inside the steel shroud as seen from the top *(middle)* and from the bottom *(right)*.

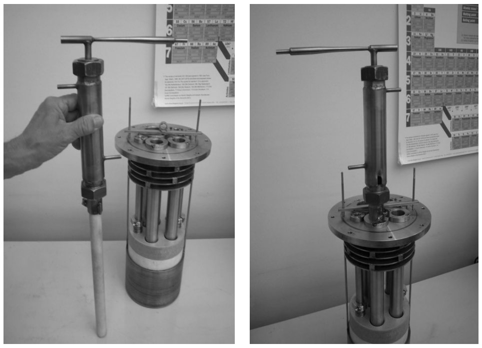
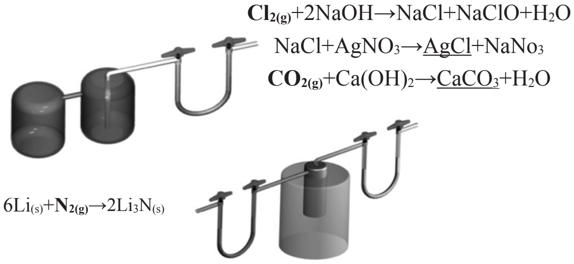


Fig. 8. Gas trapping system.



$\mathbf{Cl_{2(g)}}+2NaOH \rightarrow NaCl+NaClO+H_2O$

$NaCl+AgNO_3 \rightarrow \underline{AgCl}+NaNo_3$

$\mathbf{CO_{2(g)}}+Ca(OH)_2 \rightarrow \underline{CaCO_3}+H_2O$

$6Li_{(s)}+\mathbf{N_{2(g)}} \rightarrow 2Li_3N_{(s)}$

Fig. 11. Detection of chlorine and carbon anidride *(top)*, and nitrogen *(bottom)* generated by pyro experiments and transferred outside the glove-box through GTS.

Fig. 9. Venturi tube.

layer by powder injection plasma spraying process (PIP-SP), followed by a layer of silica applied by plasma enhanced chemical vapour deposition (PECVD), the protection proved uneffective after a forthnight of experimental campaign (Figure 7).

A further device has been added in order to improve the performance of the plant: the gas trapping system, GTS (Figure 8), which allows to "capture" and remove the gases generated during electrorefining and/or electroreduction experiments, like chlorine, nitrogen, oxygen, carbon oxide and carbon anidride. The GTS consists of a shroud made of an alumina tube connected to a stainless steel tube joined to a Venturi tube in the upper part (Figure 9) [5].

As the gas removal system will entrain salt vapors, the latter must be removed to prevent plugging and protect downstream equipment. To this end, the stainless steel tube of the shroud is internally equipped with a trap (Figure 10) to condense salt vapors on the cooled surface in a controlled process. The surface is actively cooled by a flux of argon gas which flows inside the trap and then reaches the Venturi tube. So, on one hand, it promotes condensation of the salt vapors, and, on the other hand, it allows to remove gases from the electrorefiner by creating the Venturi effect.

The gas brought outside the glove-box can be monitored or simply revealed by chemical reactions (Figure 11). In particular, chlorine and carbon anidride pass through two Drechsel bottles and react giving rise to silver chloride and calcium carbonate. Nitrogen gas, on its own, reacts with lithium beads and forms lithium nitride.

2.1 Experimental Tests

An experimental campaign has been conducted under inactive conditions by transferring Lanthanum metal from

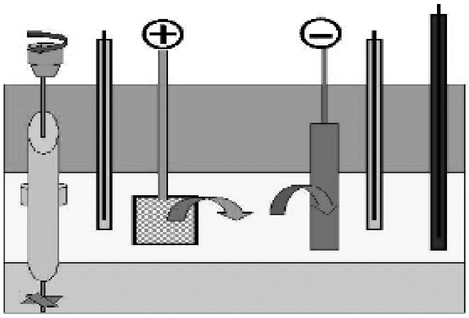


Fig. 12. Schematic of the direct transportation experiment of La ingots from FDB to SSC, also showing the guiding-tube for thermocouples, the two reference electrodes(Ag/AgCl), and the stirrer.

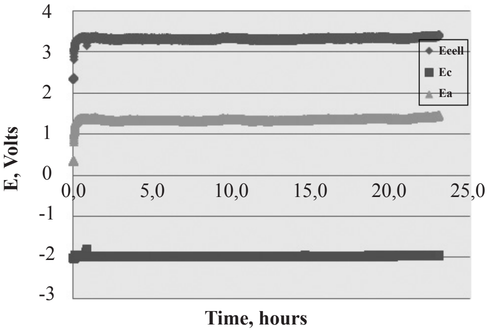


Fig. 13. Typical trend of the potentials recorded during an experiment of direct transportation of Lanthanum from FDB to SSC (E_{cell}: cell potential; E_a: anode potential; E_c: cathode potential).

the fuel dissolution basket, FDB, to the solid steel cathode, SSC, according to Figure 12. To this purpose, FDB loaded with La ingots has been immersed into the bath containing lanthanum trichloride, then a direct current has been applied between the electrodes.

The experiments had a duration of about 23 hours and were made under galvanostatic conditions. Currents from 50 to 100 mA have been applied, with current densities in the range 5.53 - 18.44 mA/cm^2/wt% La. The theoretical yield varied from 1.99 to 3.82% and the Faradic yield from 5.07 to 17.59%. Cell potentials (E_{cell}) were recorded together with anode (E_a) and cathode (E_c) potential. A typical trend is shown in Figure 13. The weight of Lanthanum in the cathode deposit was between 38 and 382 mg, corresponding to a wt% of Lanthanum of 3.81 and 10.42 respectively. Therefore, most of weight deposit is given by deposition of salt (Figure 14). Furthermore, the deposits were characterized by high porosity (see Figure 14). Cathodes of different diameter (8, 12, and 20 mm) were used. The bath of molten salt was normally stirred at 70 revolutions per minute, RPM, during the experiments.

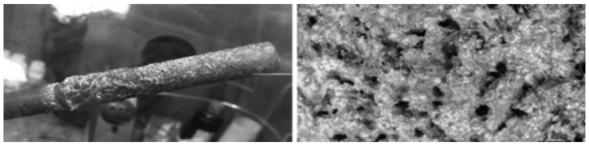


Fig. 14. Solid cathode with deposit at the end of an experiment *(left)*; detail at the stereomicroscopy of the cathode deposit, showing high porosity *(right)*.

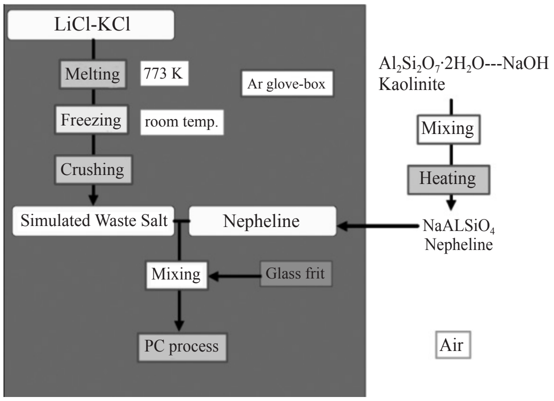


Fig. 15. Synthesis of sodalite from nepheline.

3. Conditioning of Chloride Salt Wastes

3.1 Conditioning with Sodalite

Experimental activities on conditioning of chloride salt wastes coming from pyroprocesses have been finalized to demonstrate the feasibility of sodalite synthesis through a process (Pressureless Consolidation) recently proposed by Idaho National Laboratory in USA [6].

Experiments have been made at a laboratory scale, starting from a homogeneous powder of nepheline, chloride salts and glass frit (Figure 15) [7].

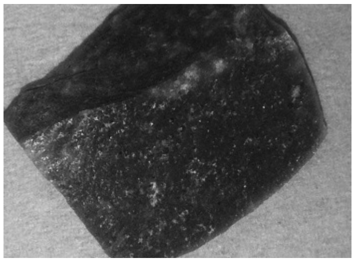


Fig. 16. Sodalite blended with glass frit after heating at 925°C for 7 hours.

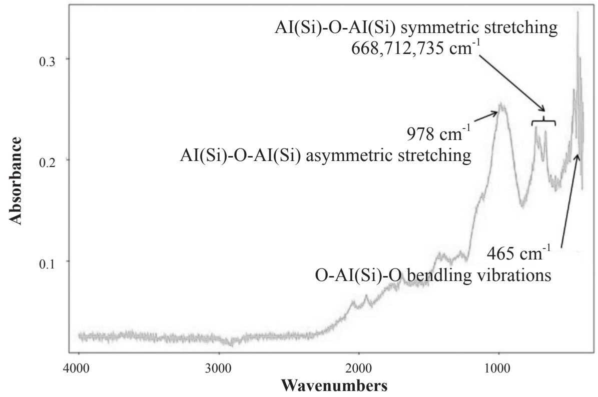


Fig. 17. FITR spectrum of Sodalite blended with glass frit after heating at 925°C for 7 hours.

Such a mix was put into an alumina crucible and slightly pressed with another alumina crucible of a smaller diameter, inside which a stainless steel bar of about 280 g had been inserted. The entire assembly was introduced in a furnace inside an argon-atmosphere glove-box. The furnace temperature was then raised at 10°C/min to 500°C and kept for about one hour, allowing the evaporation of any residual moisture. The temperature was then raised to 925°C for 7 hours. The final waste form (Figure 16) shows a density of 2.382 g/cm^3, satisfactory if compared with that reported for pure sodalite (2.1-2.3 g/cm^3).

SEM analyses and stereomicroscopy observations show the absence of both microcracks and macroporosity. As shown in Figure 17, FTIR spectrum of the final sample shows the typical peaks of sodalite at 465 cm^{-1} [O-Al(Si)-O bending vibrations], 668, 712 and 735 cm^{-1} [Al(Si)-O-Al(Si) symmetric stretching], and 978 cm^{-1} [Al(Si)-O-Al(Si) asymmetric stretching]. Coherently, XRD analysis highlighted the presence of sodalite as the main phase and of nepheline in traces.

Table 1. Normalized releases (g/m^{-2}) of sodalite samples after 7 days leaching at 90 ± 2°C

Element	Normalized release	
	This study	INL
Li	0.614	0.59
Na	0.752	0.39
Al	0.087	0.045
Si	0.157	0.047
K	0.889	0.226
Rb	0.491	
Sr	0.005	
Cs	0.451	
Ba	0.005	
La	0.005	
Nd	0.005	

Leaching tests under static conditions were performed according to the ASTM C1285-02 procedure [8]. The concentrations of the elements in the leachates, measured by ICP-MS, are reported in Table 1. The leaching behavior of sodalite blended with glass frit is comparable to that of similar glass-based confining matrices reported in the literature. To this purpose Table 1 compares the normalized release with the data by Idaho National Laboratory [9].

3.2 Conditioning with SAP Matrix

A novel method proposed by Korea Atomic Energy Research Institute (KAERI) is also applied to the treatment of chloride salt wastes [10,11]. It is based on a matrix, SAP ($xSiO_2$-yAl_2O_3-zP_2O_5), synthesized by a conventional sol-gel process (Figure 18), able to stabilize the volatile salt wastes owing to the formation of metalaluminosilicates, metalaluminophosphates and metalphosphates.

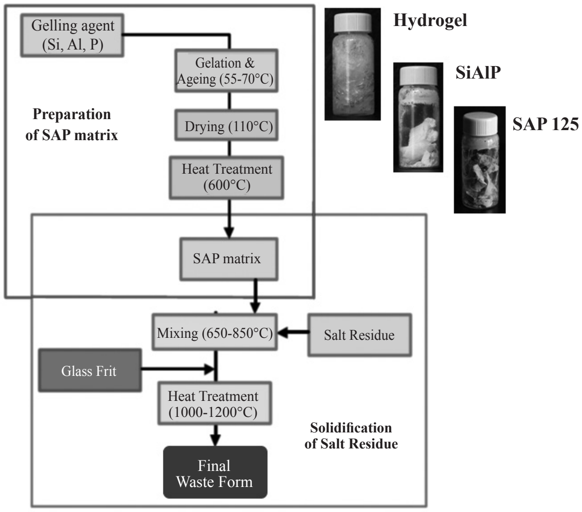


Fig. 18. Outline of the SAP process.

The addition of a glass powder as a chemical binder and a treatment at around 1150°C gives the final waste form. With this method a higher disposal efficiency and a lower waste volume can be obtained.

LiCl-KCl melt containing chlorides of alkaline, alkaline-earth metals, and lanthanides has been used to simulate the waste salt. The composite SAP has been prepared by a sol-gel process, using tetraethyl ortosilicate (TEOS), aluminum chloride ($AlCl_3.6H_2O$) and phosphoric acid (H_3PO_4) as sources of Si, Al, and P, respectively. All reagents were dissolved in $EtOH/H_2O$ and the mixture, tightly sealed, was placed in an electric oven at 70°C. After a gelling/ageing for 3 days, the transparent hydrogels were dried at 110°C for 2 days and then thermally treated at 600°C for 2 hours. The so-obtained SAP has a density of 2.291 g/cm^3. SEM investigations highlighted a morphology similar to that observed for SAP samples reported in the literature [9], as shown in Figure 19 [12].

A series of final products (SAPs) were reacted with metal chlorides at 950°C for 30 hours inside an Ar-atmosphere glove-box, after mixing them at a SAP/metal chloride mixing ratio of 2.

XRD (Figure 20), FTIR and Raman spectra of samples at increasing temperatures indicated, for temperatures

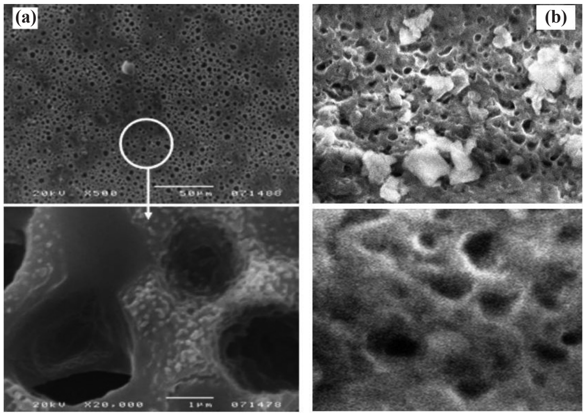


Fig. 19. Comparison of SEM pictures of SAP samples prepared by KAERI (a) and by ENEA (b).

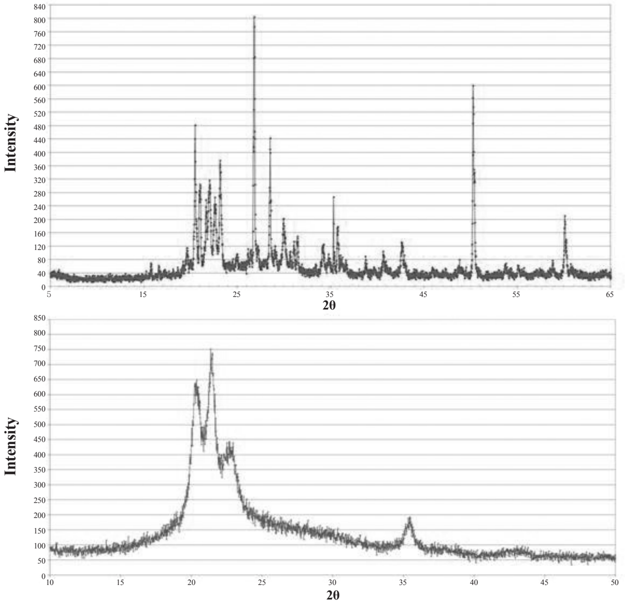


Fig. 20. XRD spectra of SAP sample *(bottom)* and of the final product *(top)*.

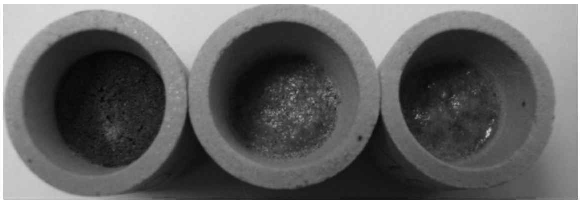


Fig. 21. Salts/SAP samples obtained after blending with glass frit and heating at 1150°C for 4 hours.

Table 2. Normalized releases (g/m^{-2}) of SAP samples after 7 days leaching at 90 ± 2°C

Element	Normalized release
Li	0.307
Na	0.328
Al	0.080
Si	0.015
K	0.127
Rb	0.095
Sr	0.004
Cs	0.039
Ba	0.002
La	0.0004
Nd	0.0003

above 850°C, the presence of peaks which can be assigned to metal-aluminosilicate, metal phosphate and metal-aluminophosphate.

The reaction products were mixed with glass powder at a mixing ratio of 70 (gel product) : 30 (glass) by weight and heat treated at 1150°C for 4 hours without pressing (Figure 21).

As expected, XRD analysis indicated an amorphous matrix with a few peaks which can be attributed to aluminum phosphate, while FTIR spectra highlighted the presence of three basic bands characteristic of the silicate-phosphate glasses.

Static leaching tests [8] on the Salts/SAP samples revealed the interesting behavior of such matrix: after 7 days leaching the concentrations of salt elements in the leachates, reported in Table 2, were lower than those obtained with sodalite.

4. Conclusions

A new facility has successfully been installed at ENEA laboratories for pyrochemical process studies under inactive conditions. Pyrel III pilot plant allows to perform experiments about electrorefining and electroreduction of simulated fuel. Moreover, an argon-atmosphere glove-box is used for conditioning of chloride salt wastes with sodalite or SAP matrix.

The data obtained from the experimental activities will give a useful contribution to the comprehension of the phenomena involved and to the improvement of the project design of industrial plants.

Acknowledgements

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