

MOLTEN SALT OXIDATION AS A TECHNIQUE FOR DECOMMISSIONING - SELECTION OF LOW MELTING POINT SALT MIXTURES

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ABSTRACT

During the 70 and 80 years, IPEN built several facilities in pilot scale, destined to the technological domain of the Nuclear Fuel Cycle. In the nineties, radical changes in the Brazilian nuclear policy determined the interruption of the activities and the shut-down of pilot plants. Nowadays, IPEN has been facing the problem of the dismantling and decommissioning of its Nuclear Fuel Cycle old facilities. The facility CELESTE-I of the IPEN is a laboratory where reprocessing studies were accomplished during the decade of 80 and in the beginning of the 90s. The last operations occurred in 92-93. The research activities generated radioactive wastes in the form of organic and aqueous solutions of different compositions and concentrations. For the treatment of these liquid wastes it was proposed a study of waste thermal decomposition based on the molten salt oxidation process. Decomposition tests of different organic wastes have been performed in laboratory equipment developed at IPEN, in the range of temperatures of 900 to 1020°C, demonstrating the complete oxidation of the compounds. The reduction of the process temperatures would be of crucial importance. Besides this, the selection of lower melting point salt mixtures would have an important impact in the reduction of equipment costs. Several experiments were performed to determine the most suitable salt mixtures, optimizing costs and melting temperatures as low as possible. This paper describes the main characteristics of the molten salt oxidation process, besides the selection of salt mixtures of binary and ternary compositions, respectively Na₂CO₃ - NaOH and Na₂CO₃ - K₂CO₃ - Li₂CO₃.

1. INTRODUCTION

Decommissioning is the final phase in the life-cycle of nuclear facilities, after sitting, design, construction, commissioning and operation. The final objective of decommissioning operations is the unconditional release or reuse of sites, facilities, installations or materials for other purposes. It is a process, which involves operations such as decontamination, dismantling of plant equipment and facilities, demolition of buildings and structures, and management of the resulting materials. All of these activities take into account the health and safety requirements of the operating personnel and the general public, and also any implications these activities have for the environment. Every decommissioning strategy should include an approach in order to minimize the production of radioactive wastes. The aim of a waste minimization strategy is to maximize the opportunities for release or

recycle/reuse of materials, and when residual radioactive wastes are unavoidable, to minimize their volumes for storage and disposal [1].

Nowadays, the decommissioning of nuclear facilities is of great interest because of the large number of facilities which were built many years ago and which will have to be shut-down from service in the near future [2]. As a result of these decontamination and decommissioning (D&D) operations, a wide range of materials arise. Radioactively contaminated materials arise from the decommissioning of all nuclear facilities. When decommissioning nuclear facilities, some of the materials will be radioactive as a result of activation and/or contamination. In general, a large amount of the materials will be inactive, which means that they will be available for unconditional release.

During the 70 and 80 years, IPEN built several facilities in pilot scale, destined to the technological domain of the Nuclear Fuel Cycle. In the nineties, radical changes in the Brazilian nuclear policy determined the interruption of the activities and the shut-down of the pilot plants. Nowadays, IPEN has been facing the problem of the dismantling and decommissioning of their Nuclear Fuel Cycle old facilities. The facility CELESTE-I of the IPEN is a laboratory where reprocessing studies were accomplished during the decade of 80 and in the beginning of the 90s. The last operations occurred in 92-93. The research activities generated radioactive wastes in the form of organic and aqueous solutions of different compositions and concentrations. Part of the wastes generated during the operations is stored under hot cell. For the future treatment of these liquid wastes it was proposed a study of waste thermal decomposition based on the molten salt oxidation process.

2. MOLTEN SALT OXIDATION PROCESS FOR WASTES DECOMPOSITION

An alternative to the incineration for the treatment of a vast range of dangerous residues is the decomposition through the submerged oxidation in molten salt baths. Stelman and Gay [3] compare the characteristics of the conventional incineration and the decomposition of wastes in molten salts. In spite of being a thermal decomposition process, molten salt oxidation is not considered an incineration process. Differently of the incineration, the process doesn't request a flame to begin or to continue the reaction.

Navratil and Stewart [4] describe results obtained in the destruction of different types of residues. Among the wastes that can be destroyed satisfactorily through this technique, the following could be stand out: PCBs, hospital wastes, propellants, explosives, chemical and biological war agents, fireworks, reduction of the volume of mixed radioactive wastes of low activity, gases, oils, plastics, pesticides, etc.

The molten salt oxidation was developed in the fifties by the Rockwell International Co. for U.S. Atomic Energy Commission using molten fluorides. Initially, it was developed for activities of the nuclear fuel cycle not related to the wastes. Later, experiments were accomplished for removal of sulfur dioxide from gases of the coal combustion and as catalyst of the coal gasification. The experiments used molten sodium carbonate. Due to the capacity of the process to rust completely organic materials, Rockwell Int. tried the oxidation of dangerous organic residues, but the activity was interrupted in 1982 [5]. Due to the existence of less onerous technologies of waste incineration, tendency to storage wastes instead of disposing them and less severe environmental concerns regarding the dangerous products of

the incineration, the development of the technique stayed stagnated practically until the nineties.

The molten salt oxidation - MSO - consists of a submerged thermal decomposition of organic materials. It allows the immediately oxidation of the hydrocarbons molecules to carbon dioxide and water in the steam form. In this process, the waste and the oxidizer (usually air) are mixed in a turbulent bed of salts in melted state. The conditions of the oxidation in molten salts provide lower process temperatures than those used in the incineration. The low temperatures, associated to the liquid phase in that the reactions occur, allows a significant reduction in the production of nitrogen oxides, besides the retention of inorganic components, and even radioactive materials, in the saline bath. The salt, being of alkaline nature, "washes" and neutralizes any acid gases as, for instance, the sulfuric and hydrochloric acids, eventually produced in the oxidation process.

In the molten salt oxidation, a molten alkaline salt as, for instance, sodium carbonate - Na_2CO_3 - acts as catalyst of the conversion of an organic material and oxygen in water and carbon dioxide. Acid species are kept in the bath as inorganic salts, instead of their releasing as gases or particulate matters in the atmosphere. Metallic elements, radioactive or not, react with the molten salt and the oxygen, forming metallic oxides that are kept in the bath as ashes. In this way, a gas scrubbing equipment is not necessary, and consequently no liquid waste is generated in the process. The technique could be described, in a simpler manner, as a simultaneous process of oxidation and scrubbing of the reaction products. This can be obtained by the injection of the material to be burned and air in excess below the surface of a melted salt, or melted salt mixtures as, for instance, sodium carbonate and sodium sulfate, maintained in temperatures in the range from 900°C to 1000°C . This process does not involve the combustion with the formation of a flame. Because of the catalytic action of the salts, the oxidation happens second a pattern that can be defined as of liquid phase. The salts are not consumed in the process, except in the case of decomposition of wastes containing halogens atoms, like chlorides, for instance. In this case, it is formed sodium chloride by the reaction of the chlorine and the sodium of the salt. This is an intrinsically important characteristic of the molten salt oxidation, since the dioxin and furans formation is avoided by the mentioned reaction. The gases introduced or generated in the process are forced through the saline bath before leaving the equipment, what provides a wash action. Among several advantages, such as oxidative reactions that transform completely the components of the organic waste in just CO_2 and water, the process equipment can be built in small scale. For their chemical characteristics and of project, the formation of dioxins and furans can be neglected.

Therefore, the molten salt oxidation provides much more efficient thermal decomposition of hazardous organic wastes than the incineration. Some wastes from nuclear facilities, such as: n-tributyl phosphate, ionic change resins, silicon carbide, gloves containing lead can be also destroyed in an efficient and safe way [6]. In the Fig. 1 a schematic drawing of the process is presented.

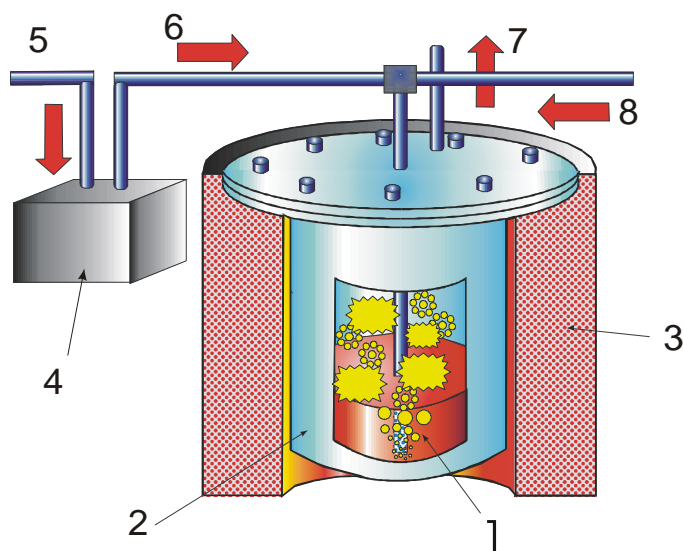


Figure 1: Schematic drawing of the molten salt oxidation process where 1- molten salt, 2 – reactor vessel, 3- heating system, 4- wastes pressurized reservoir, 5- compressed air, 6- waste feeding piping, 7- Off gas, 8- Air/oxygen injection.

3. MOLTEN SALT EQUIPMENT DEVELOPED AT IPEN AND IMPROVEMENTS

Several decomposition tests of different organic wastes have been performed in laboratory equipment developed at IPEN, in the range of temperatures of 900 to 1020°C, with excellent results. The completeness of the oxidation reactions was evaluated by mass spectrometry of the gases released. The molten salt after cooling can be dissolved in water for uranium and plutonium recovering as a mixture of oxides by filtering (U_3O_8 , PuO_2 and oxides of metals such as Ni, Cr and Fe from the reactor vessel corrosion). As the molten salt (sodium carbonate) in the range of temperatures studied (900 to 1020°C) is very corrosive, the reactor vessel must be constructed with an expensive nickel alloy – Inconel™ 600. The developed equipment can be observed in the Fig. 2.



Figure 2: Heating system and reactor vessel (left), molten salt (center), reactor with molten salt removed from the heating system.

Nevertheless, considering the purposes of the research project and the presence of Pu in the wastes, it was necessary to develop a smaller reactor / heating system, compatible with the dimensions of one glove-box. In the Fig. 3 are presented pictures of the new reactor.



Figure 3: Comparison between the two reactors (left), reactor and its heating system (right).

The smaller reactor was adapted to a small glove-box with the objective of evaluating the interferences and difficulties associated. Later, the equipment will be set up in a glove-box inside the CELESTE-1 Laboratory. In the Fig. 4 the assembling of the conjunct heating system / reactor in the glove – box can be observed.



Figure 4: Assembling of equipment inside glove-box.

Some tests were accomplished to evaluate the equipment. It was necessary to increase the thermal insulation to avoid damage to the glove-box acrylic walls. Another problem verified is a consequence of the reactor dimensions. It was verified that the reactor vessel height must be increased to avoid solidification of the salt in the upper reactor region (flange). The molten

salt was carried by the gases. It solidified and obstructed the passage of the gases from the waste decomposition, as it can be observed in the Fig. 5. This problem limited the flow rate range of waste and oxidant gases tested during the experiments.



Figure 5: Clogging of salt solidified in the upper region of the reactor (left), molten salt can be observed through the central hole left by the injection lance (right).

In spite the mentioned problems, the process feasibility has been demonstrated. Nevertheless, it will be necessary to introduce some modifications in the equipment to permit its assembling inside a glove-box, such as increasing of the reactor height, improving the thermal insulation of the heating system and a larger glove-box. As the reactor material is expensive, the modifications could yet not be implemented. However, a new glove-box has been selected and it could receive a small molten salt reactor for future decomposition of the wastes, as it can be observed in the Fig.6. The tests accomplished will permit to build in the future a optimized equipment for decomposition of the U and Pu solutions stored in the hot cell tanks and flasks, considering the needs of the facility dismantling and decommissioning.



Figure 6: A larger glove-box, previously used in the process (already contaminated) could be used for future assembling of the molten salt equipment.

4. REDUCTION OF THE PROCESS TEMPERATURE

The high temperatures involved in the decomposition of wastes are a problem in case of processes performed inside glove-boxes. Nevertheless, the use of glove-boxes is necessary for the radioactive wastes mentioned. Then, the reduction of the process temperatures would be of crucial importance. Besides this, the selection of lower melting point salt mixtures would have an important impact in the reduction of equipment costs. Several experiments were performed to determine the most suitable salt mixtures, optimizing costs and melting temperatures as low as possible. Some experiments were performed for the selection of salt mixtures of binary and ternary compositions, with a reduced melting point in comparison with the pure sodium carbonate. The saline bath investigated consisted of pure sodium carbonate, whose melting temperature is 851 °C. The selected binary and ternary salt mixtures were respectively Na₂CO₃ - NaOH and Na₂CO₃ - K₂CO₃ - Li₂CO₃. Several fusion tests were performed to evaluate the melting temperature of salt mixtures with different contents of each component.

As the use of pure sodium carbonate prevents the execution of the process below the melting temperature of 851 ° C, other salt mixtures were investigated such as eutectic mixture of sodium carbonate and sodium hydroxide, whose melting temperature is 286 ° C (41% sodium carbonate and 59% sodium hydroxide solution - percentages by mass) and mixtures of carbonates of sodium, lithium and potassium with melting temperatures bellow of that of pure sodium carbonate.

Thus, tests were performed to determine the salt mixture with a lower melting temperature to be used in the oxidation process. However, in addition to reducing of the melting temperature, the salt mixture used must be compatible with the material of the reactor, in order to not cause rapid corrosion of components. In these experiments the following salts were used: Li₂CO₃, Na₂CO₃, NaOH, K₂CO₃, an analytical balance, a beaker of 250 mL, a crucible of stainless steel, a muffle furnace, a form of metal, a thermocouple type K (chromel-alumel) and a voltmeter.

For selection of salt mixtures, fusion tests were performed with different compositions, using a muffle furnace and a crucible. The crucible has a pit in its lower portion, consisting of a closed tube, in which is inserted a thermocouple for measuring the temperature of melting / solidification of the selected salt mixtures. In Fig. 7, it can be observed the crucible with the thermocouple pit/tube, the same crucible heated inside the muffle furnace and salt mixtures of different compositions.

The masses of each component were weighed according to the desired percentage for each salt mixture, both in secondary mixture of salts (NaOH and Na₂CO₃), and for the tertiary mixture (Li₂CO₃, Na₂CO₃ and K₂CO₃). The total mass of each mixture of salts (for each experiment) was approximately 300g, placed in a beaker, subsequently transferred to the crucible, which was placed in the muffle furnace at 700°C, for complete fusion of each salt mixture. After the time required for fusion of the salt mixture, with aid of the voltmeter, it was possible to measure the voltage caused in the thermocouple at the time the salt began to solidify and through the thermocouple conversion table, the voltage was associated with an approximate temperature of melting/solidification of the salt mixture, obtained experimentally.

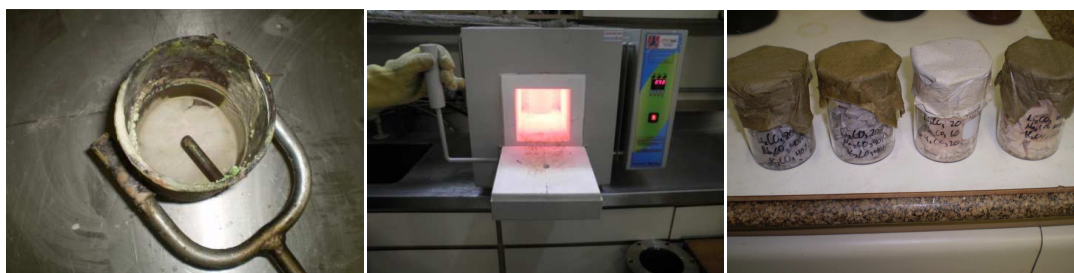


Figure 7: Crucible with pit/tube for thermocouple, muffle and some salt mixtures tested.

Tests were made varying concentrations of sodium hydroxide and sodium carbonate. The percentages were: 40%, 50%, 60%, 70 mass% sodium hydroxide corresponding, respectively, to the percentages of 60%, 50%, 40%, 30% by weight of sodium carbonate. Tests were also performed by mixing Li_2CO_3 , Na_2CO_3 and K_2CO_3 with different proportions of the three components. The test results of some selected compositions of salts for fusion are presented in Table 1.

Table 1: Results of tests to determine experimentally the melting temperatures of some pre-selected salt mixtures.

Salt Mixture	Mass ratio of components A, B and C			
	30A-70B	40A-60B	50A-50B	60A-40B
$\text{Na}_2\text{CO}_3\text{-NaOH}$				
Melting temperature °C	238	254	264	318
$\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$				
Melting temperature °C	452	412	402	492

5. CONCLUSIONS

Melting tests were carried out with different salt mixtures compositions to optimize the melting temperature as low as possible and at acceptable costs, since lithium carbonate has a significantly higher price than other carbonates. The melting temperatures of the mixtures of salts vary widely depending on the composition, which in turn is related to the ions load, i.e. the greater the ion load the higher the melting temperature. In other words, it will require less energy to separate (and to melt) a salt compound with an ion charge of 1+ than a salt with an ion charge of 2+.

Although the mixture of sodium carbonate-sodium hydroxide has provided low melting temperatures (even below 300°C) in tests for compatibility with the Alloy 600, the mixture proved to be very aggressive in terms of corrosion, quite beyond the expected and acceptable. In the Fig. 8, it can be observed the corrosion of the lance tube made of Alloy 600 after some hours at temperatures of 900°C.



Figure 8: Open molten salt mixture reactor (left), lance tube after 12 hours of immersion in the sodium carbonate-sodium hydroxide salt at 900°C, and the lance tube after 72 hours at the same temperature.

In corrosion tests, the material degradation was accelerated, causing the exclusion of this composition for the subsequent decomposition tests. The attack mechanism is not yet understood, but it must be associated with the presence of OH-ion, probably deleterious to nickel, the main constituent of the alloy (with more than 75% by mass).

The mixture of carbonates of sodium, potassium and lithium, although less aggressive than hydroxide does not allow obtaining such low temperatures. The eutectic composition is 32% by mass of lithium carbonate, 35% by weight of potassium carbonate and 33% sodium carbonate, with melting temperature of 397 ° C [7]. It has low corrosiveness, low toxicity and high thermal stability.

As a conclusion of the melting experiments, a mixture of Li_2CO_3 , Na_2CO_3 and K_2CO_3 , with the respective proportions in mass of 20A-60B-20C, was chosen for the subsequent waste decomposition tests. The binary mixtures of sodium carbonate and sodium hydroxide, despite their lower melting temperatures, showed a very marked and unexpected corrosion to the Alloy 600 and because of this they were rejected for the waste decomposition tests.

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