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THERMAL DECOMPOSITION OF CONTAMINATED ORGANIC SOLUTIONS USING MOLTEN SALT OXIDATION – PRELIMINARY DEVELOPMENTS

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ABSTRACT

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 decade of 90. The research activities gave origin to radioactive wastes in the form of organic and aqueous solutions of different compositions and concentrations. Part of the wastes generated during the operations accomplished in the CELESTE-I Laboratory is stored in waste special reservoirs, under the hot cell. The wastes contain U, Pu, Np, Am, HNO_3, TBP (tri-n-butil phosphate), hexone and TTA (tenoiltrifluoracetone). Besides this, there are also stored in the facility several flasks containing considerable volumes of different liquid wastes from analytical procedures of U determination, containing U, HNO_3, TBP, hexone, pyridine, aluminum and DBM (dibenzoilmetane). The volume of organic and aqueous solutions stored in the tanks and flasks in the facility is about 470 liters. As the treatment of this kind of liquid wastes is complex (the incineration, for example, is not possible), we proposed a study of a thermal decomposition process. This process has already been developed in IPEN, in a laboratory scale, and it is based on the submerged oxidation in a molten salt bath. Among several advantages, such as oxidative reactions that transform completely the components of the organic solvent in just CO_2 and water, the process equipment can be built in such small scale, compatible with the space available, for example, in hot cells or glove boxes. The process admits water content in the organic solution of about 20 % without problems. This paper describes the molten salt oxidation equipment totally built in the IPEN and the results of the decomposition of different organic wastes (dichlorethane, dichlorodifluoromethane and toluene).

1. INTRODUCTION

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 decade of 90. The last operations performed occurred in 92-93. The research activities gave origin to 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. Facility pictures can be observed in the figure 1 and a schematic drawing is presented in the illustration 2, showing the waste tanks.

The liquid wastes were generated during the process operations accomplished in the CELESTE-I Laboratory. The wastes that were stored in the facility waste tanks are from plutonium retention studies in columns. The wastes contain U, Pu, Np, Am, HNO_3, TBP (tri-n-butil phosphate), hexone and TTA (tenoiltrifluoracetone).

Some wastes, from colorimetric and potentiometric analytical procedures, are stored in glass flasks, inside glove-boxes or under hoods. These wastes, containing U, Pu and Am, were used in chromatographic extraction studies. Besides this, there are also stored in the facility several flasks containing considerable volumes of different liquid wastes from analytical procedures of U determination, containing U, HNO_3, TBP, hexone, pyridine, aluminum and DBM (dibenzoilmetane).

The volume of organic and aqueous solutions stored in the tanks and flasks in the facility is about 470 liters. As the treatment of this kind of liquid wastes is not possible now in IPEN, we proposed a study of a waste thermal decomposition process. It was proposed a study based on the process of submerged oxidation of wastes in a molten salt bath.

Figure 1: Hot cells of the CELESTE-1 laboratory.

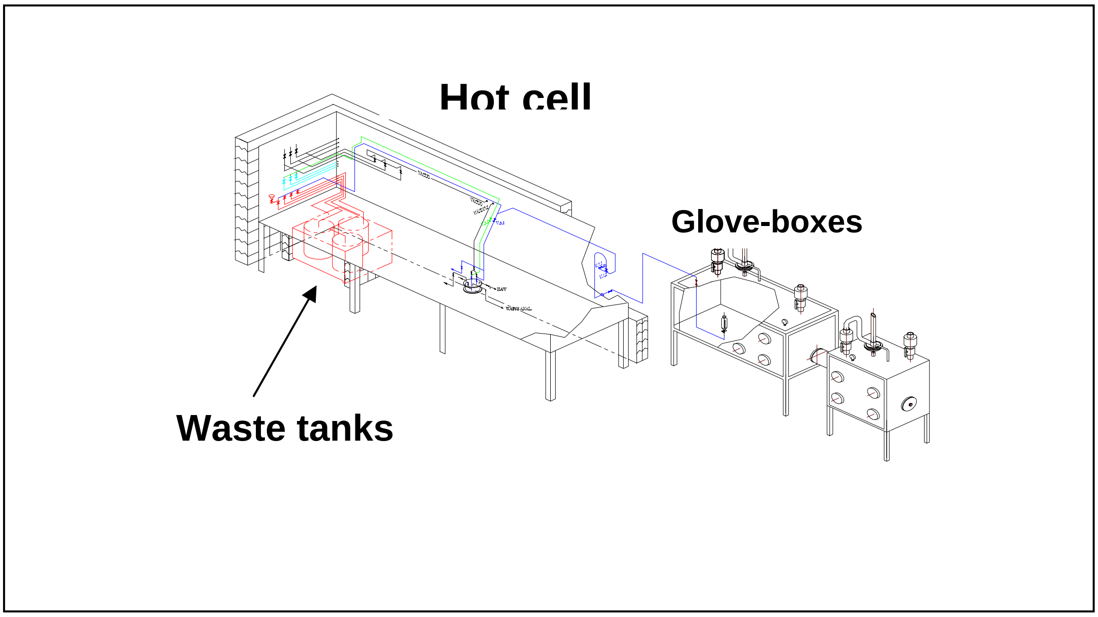

Figure 2: Hot cells schematic drawing and tanks.

The interest in the decomposition of hazardous wastes by advanced methods, as alternative to the incineration and, and specially through the molten salt oxidation elapsed mainly of a specialist's suggestion, Dr. James Navratil (at that time, linked to the Idaho National Engineering and Environmental Laboratory - INEEL / US DOE), in a Technical Visit to IPEN, sponsored by the International Agency of Atomic Energy - IAEA.

2. MOLTEN SALT OXIDATION OF ORGANIC WASTES

In the last decades, there were significant changes in the perception of the necessity of environmental preservation. The main actions that have been used to impede the migration of pollutants to the environment are: the inventory of the hazardous chemical compounds, their safety collection and their suitable treatment. One of the predominant concepts currently is that the wastes should be destroyed in some point of their cycle of use, specially the dangerous ones, in reason of the risk that they represent for human beings, animals and plants. The worldwide interest in the development of advanced decomposition technologies of wastes elapses, mainly, of the problems created by the denominated POPs - persistent organic pollutants. The thermal decomposition has been commercially used in the disposal of hazardous wastes, mainly the incineration, whose most important characteristic is the combustion with flame. However, the incineration technologies have failed to meet some performance criteria. An alternative to the incineration, for the treatment of a vast range of dangerous wastes or not, it is the thermal decomposition by means of the submerged oxidation in molten salt baths. Experience in this technique did not exist at IPEN, nor have references been found about its use in Brazil. One of the objectives of this work was the conception, construction and the development of equipment with this purpose. During the program the selection and the performance tests of the employed materials, the construction of components and auxiliary systems, their assembly and the operational tests have been carried out [3].

Among several advantages, such as oxidative reactions that transform completely the components of the organic solvent in just CO_2 and water, the process equipment can be built in such small scale, compatible with the space available in the hot cells. The process admits water content in the organic solution of about 20 % without problems. Molten salt oxidation equipment has already been built at IPEN and different organic wastes have been tested (dichlorethane, dichlorodifluoromethane and toluene). In the figure 3 a schematic drawing of the process is presented.

Several decomposition tests of different organic wastes have been performed in laboratory equipment developed at IPEN, with excellent results. The effectiveness of the equipment was verified with cases studied, with the attainment of data about decomposition, in molten salts, of three organic wastes: 1,2-dichloro-ethane, difluorodichloromethane and toluene. The completeness of the oxidation reactions was evaluated by mass spectrometry of the gases released. 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 expansive nickel alloy – Inconel™ 600. The developed equipment can be observed in the figure 4.

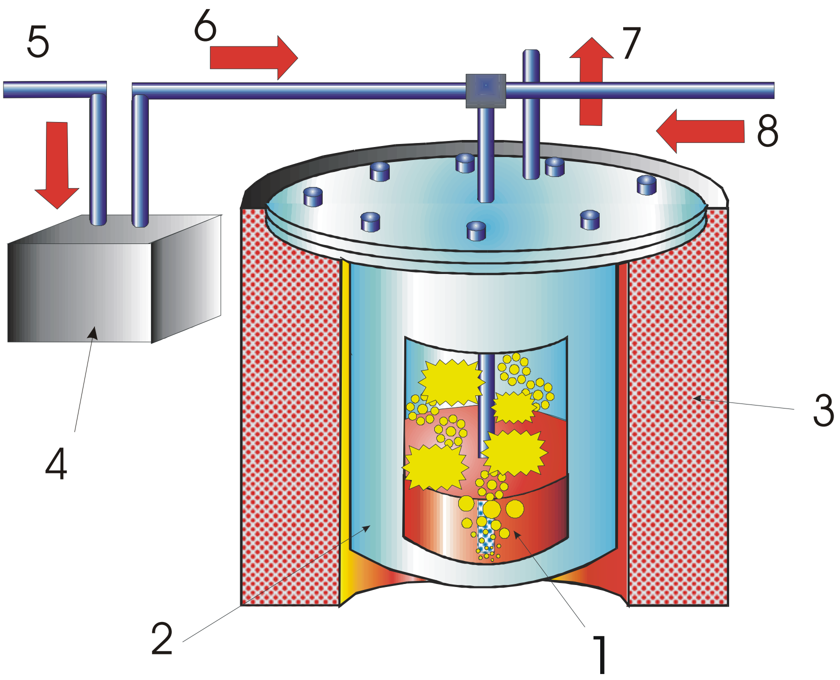

Figure 3: Schematic drawing of the molten salt oxidation process where 1- molten salt, 2 – reactor vessel, 3- heating system, 4- wastes pressurized reservoir, 5- compressed air, 6- waste feeding piping, 7- Off gas, 8- Air/oxygen injection.

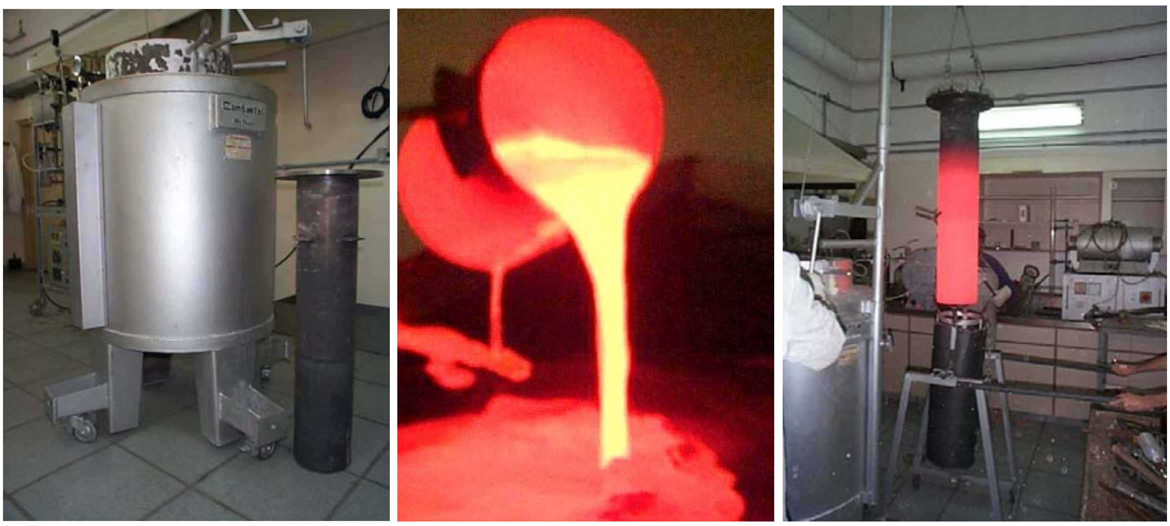

Figure 4: Heating system and reactor vessel (left), molten salt (center), reactor with molten salt removed from the heating system.

One of the process advantages is that 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). In the figure 5 is presented the salt dissolved in water and a filtering operation to U oxide recovery.

Figure 5: Dissolution of the salt and filtering to separate the present oxides.

3. CONCLUSION

Molten salt oxidation of the existent organic radioactive wastes was proven to be a reliable and feasible method of hazardous waste destruction. Analysis by CG/MS demonstrated that destruction efficiencies of 99.99986% are possible in the developed equipment. The only compounds present in the process off gases are water and carbon dioxide.

Nevertheless, considering the purposes of the research and the presence of Pu in the wastes, it is necessary to develop a smaller reactor / heating system, compatible with the dimensions of one glove-box. It will be necessary to promote some adjustments and optimize the process to operation inside glove-boxes. The smaller reactor must be adapted to a 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.

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