MOLTEN SALT OXIDATION – A SAFE PROCESS FOR HAZARDOUS ORGANIC WASTES DECOMPOSITION

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Abstract

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. The interest in the decomposition of hazardous wastes by advanced methods, as alternative to the incineration, and especially through the molten salt oxidation has elapsed mainly by the adoption of more restrictive air emissions legislations in several countries. 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 small scale. Molten salt oxidation equipment has already been built at IPEN and different organic wastes have been tested. 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. Several decomposition tests of different organic wastes have been performed in laboratory equipment developed at IPEN, with excellent results (dichlorethane, dichlorodifluoromethane and toluene). The completeness of the oxidation reactions in the range of temperatures studied (900 to 1020°C) was evaluated by mass spectrometry of the gases released. This paper describes the main characteristics of the molten salt process, besides the conception, the construction, the development of equipment with this purpose in IPEN and its effectiveness. During the activities the main accomplished tasks were the selection and the performance tests of the employed materials, the construction of components and auxiliary systems, their assembly and the operational tests carried out.

Key words: oxidation, molten, salts, hazardous, wastes.

1 Introduction

In the last decades, there were significant changes in the perception by the public of the necessity of environmental preservation. Certainly, one of the largest problems that the modern societies have faced is the disposition of some industrial residues, particularly the hazardous and dangerous wastes. 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.

The conventional incineration, whose more important characteristic is the combustion with flame, presents some restrictions as a decomposition method, taking into account the current tendency, on the part of the environmental organisms, of implanting legislation progressively more restrictive as for the emissions generated in the processes of destruction of residues. Some problems associated to the incineration elapse of the low efficiency, in molecular level, as the chemical reagent species are put in contact with the oxygen, delaying the destruction reaction [1].

Incinerators can release by the chimneys hazardous compounds, among which could be mentioned: heavy metals, organic material partially burned as polyvinyl chloride (PVC) or other products resulting of the incomplete combustion (PCIs), polycyclic aromatic hydrocarbons (PAHs) [2]. Besides, compounds extremely dangerous, such as dioxins and furans, can be formed during the gas cooling (products of the recombination of molecular fragments), demanding systems capable to reduce the temperature of the final products of the combustion very quickly. This abrupt reduction of the temperature - about 1200^{o}C to 80^{o}C in few seconds - would be a way of avoiding the formation of the mentioned compounds, demanding a rigid control of the process and special equipments - like a quencher [3]. It is known that several PAHs, dioxins and furans are cancerous agents for human beings, besides the fact that they be considered poisonous in values of parts for trillion.

As the disposition of hazardous wastes, in sanitary landfills and through incineration, has became a problem gradually more complex, because the decrease of the available space for storage or the increase of the demands of the governmental regulations, besides the increase of the public's conscience in relation to the impact of the contamination of the environment by dangerous substances, some alternative methods have been developed to convert these wastes in an appropriate way.

2 Submerged Oxidation in Molten Salts

An alternative to the incineration, for the treatment of a vast range of dangerous residues or no, it is the decomposition through the submerged oxidation in molten salt baths. Stelman and Gay [4] 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 [5] they 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 [6]. 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 the employed in the incineration. This, 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 acids and hydrochloric, 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, it is not necessary gas scrubbing equipment and, consequently, the generation of liquid wastes 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-tributil phosphate, ionic change resins, silicon carbide, gloves containing lead can be also destroyed in an efficient and safe way [7]. In the figure 1 a schematic drawing of the process is presented.

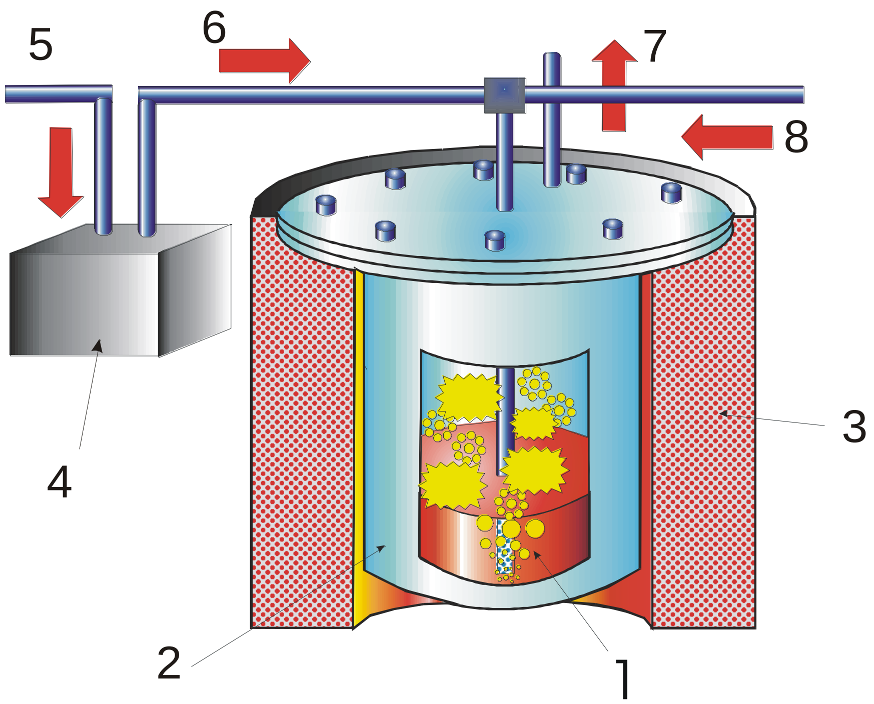

Figure 1: Schematic drawing of the molten salt oxidation process where 1- molten salt, 2 – reactor vessel, 3- heating system, 4- wastes pressurized reservoir, 5- compressed air, 6- waste feeding piping, 7- Off gas, 8- Air/oxygen injection.

3 Experimental procedure

Actually, some activities related to this process have already been performed in IPEN. Molten salt oxidation equipment has already been built. For the execution of the waste oxidation tests, it was projected and built a reduced dimensions unit (bench scale).

3.1 Construction of the reactor vessel

A fundamental problem in this development was the construction of the reactor vessel, since the operational conditions (high temperature and corrosive environment due the molten salts) determined the necessity of special materials. The construction material should present good resistance to an environment constituted by alkaline salts and, eventually, their mixtures. The alloy to be chosen should also possess good resistance to a mixture of air, water steam and carbon dioxide

The alloys with high nickel content were considered in reason of their high resistance in corrosive atmospheres, such as, for instance, the existents in chlorides or alkaline solutions. Already the presence of the chrome in the alloy provides good resistance to the oxidizing atmospheres. In the figure 2 a picture of the vessel of the reactor and a smaller prototype for performance tests can be observed. The chosen constructive material was a nickel-chrome alloy denominated commercially Alloy 600, manufactured by Philip Cornes Group. Among the main properties of this alloy it should be pointed good resistance to the oxidation at high temperatures and to corrosive in high temperatures. The maximum recommended operation temperature is 1100^{o}C and the material does not present larger difficulties in the welding. The composition of the league can be observed in the Table 1.

Figure 2: Reactor (left) and a prototype (right, smaller) for performance tests.

Table 1: Chemical composition of the Ni-Cr alloy employed in the reactor vessel.

Element (Mass %)	Ni	Cr	Fe	Mn	Cu	Si	C
Nominal	72#	14 a 17	6 a 10	1 *	0,5 *	0,5 *	0,15*
Analysis	74,2	15,5	8,9	0,2	0,1	0,1	0,01

* Maximum values # Minimal values.

In the figure 3 pictures of the molten salt and the reactor opened with the salt at approximately 1000°C can be observed. In the figure 4 it is possible to see the reactor vessel and the electric heating system, besides the hot rector removed from the heating system.

Figure 3: molten salt (left) and the rector opened (right) containing the molten salt.

Figure 4: Heating system and reactor (left), hot reactor removed from the heating system (right).

3.2 Decomposition of hazardous organic compounds

The effectiveness of the equipment was verified in terms of extent of an organic compound thermal decomposition. The evaluation was performed with cases studied, with the attainment of data about decomposition, in molten salts, of three organic wastes: 1,2-dichloro-ethane, difluorodichloromethane and toluene. Main process parameters tested during the experiments were: salt temperature, waste and air flow rates, besides the lance geometry. A gas chromatograph coupled with a mass spectrometer – CG/MS - was used to analyzing molecular fragments present in the off-gas, retained in a resin XAD-4 and eluted with n-hexan. The sampling system assembled in the off gas pipeline and the injection of a sample in the CG/MS equipment are presented in the figure 5. The results of the toluene decomposition as a function of the temperature in the range of 900°C to 1020°C can be observed in the figures 6. In the same figure it is possible to see an example of lance geometry adopted in the decomposition tests. The lance geometry controls the bubble size and this is an important parameter to promote the heat exchanges and to increase the residence time. It was reached a destruction efficiency of: DE = 99, 999986%.

Figure 5: Gas sampling system (left and center) and CG/MS analysis (right).

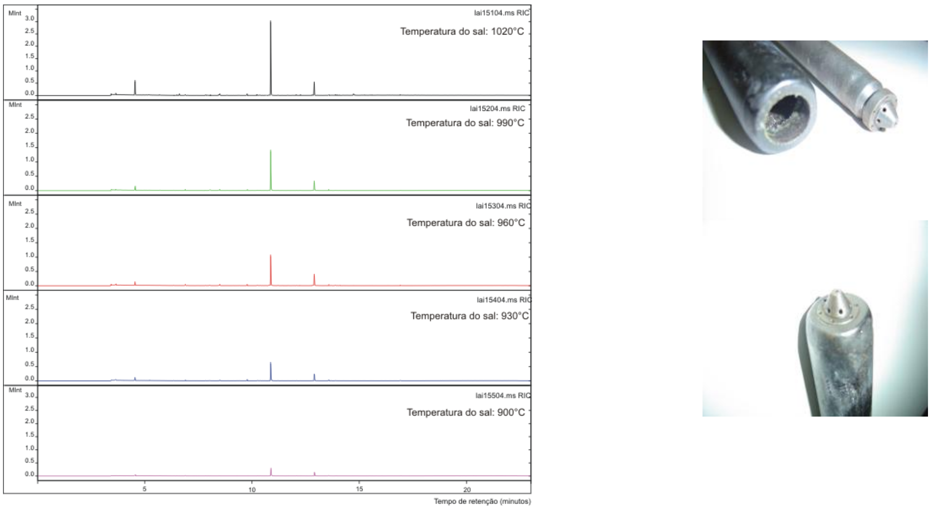

Figure 6: Results of the decomposition of toluene (left) and lance geometry (right).

4 Conclusion

The main objective of this paper was the technique description and some general results. Molten salt oxidation of organic compounds 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 most important result was the lack of molecules fragments with chloride or fluorides. In tests performed with compounds containing halogens, like chlorides (1,2-dichloro-ethane) and chlorides and fluorides (difluorodichloromethane), the only compounds present in the process off gases are water, carbon dioxide and very small amounts of hydrocarbons. With some adjustments of process parameters like, for instance, the air stoichiometric excess and optimizing the equipment it will be possible to eliminate even the small amounts of hydrocarbons.

This is a promising technique for thermal decomposition of organic materials containing Cl, F, Br. I, N, P, S. The compounds can be decomposed in a safe way in the equipment. X-ray diffraction analysis of the salt after the decomposition tests proved that Cl and F are converted in correspondent sodium salts. Then, this is a promising method for destruction of several compounds that could be considered Persistent Organic Pollutants – POPs, such as: trichloroetilene, tetrachloroetilene, trichloroetane, carbon tetrachloride, freon, nitrometane, piridine, urea, alcohol, glicol etilen, phosphate n-tributil. Solid materials can also be decomposed, since they are previously triturated. These solids include: resins of ionic change in the microspheres form, plastics ABS, granules of activated carbon, gloves and boots triturated. Some of the mentioned wastes are of special interest for the nuclear industry, since some radioactive wastes – low and intermediate level – can be treated for volume reduction. The salt retains most of the radioactive elements in the oxide form. The salt can be treated by water dissolution and filtering, with removal of the radioactive materials. The salt can be used again in the process after concentration and crystallization.

The characteristics that distinguish the molten salt oxidation of other techniques can be described concisely as: existence high coefficients of heat transfer and low temperature deviations, due the properties of the molten salt and the liquid phase where the reactions are occurring; neutralization and absorption of acid gases in the bath; retention of metals and ashes in the salt; existence of some catalytic action by the salts present in the bath. After the decomposition of the waste, the salt keeps the present metals in the compounds in the form of oxides.

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Acknowledgments

Acknowledge the support of International Atomic Energy Agency that provided funds to the Research Project - Decommissioning of Nuclear Fuel Cycle Facilities at IPEN (Brazil), Contract no. BRA-12800 and CNPQ – *Conselho Nacional de Desenvolvimento Científico e Tecnológico* / MCT – *Ministério da Ciência e Tecnologia do Brasil* for the financial support to the Project *CONSTRUÇÃO DE UM NOVO PROTÓTIPO DE EQUIPAMENTO PARA DECOMPOSIÇÃO TÉRMICA POR OXIDAÇÃO SUBMERSA EM SAIS FUNDIDOS E TESTES COM HEXACLOROCICLOHEXANO BHC*.