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Safe Degradation of the Pesticide Hexachlorcyclohexane by Molten Salt Oxidation

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Abstract: This study was motivated by the world interest in the development of advanced processes of waste decomposition, due to the need of safer decomposition processes, particularly for the POPs (Persistent Organic Pollutants) and the organochlorines. A tendency observed at several countries is the adoption of progressively more demanding legislation for the atmospheric emissions from the waste decomposition processes. The suitable final disposal of hazardous organic wastes such as PCBs (Polychlorinated Biphenyls), pesticides, herbicides and hospital residues constitutes a serious problem. In some point of their lifecycles, these wastes should be destroyed, in reason of the risk that they represent for the human being, animals and plants. The process involves a chemical reactor containing molten salts, such as sodium carbonate or some alkaline carbonates mixtures to decompose the organic waste. The decomposition is performed by submerged oxidation. Waste is injected below the surface of a turbulent salt bath along with the oxidizing agent. Decomposition of halogenated compounds, among which some pesticides, is particularly effective in molten salts. The process presents properties such as intrinsically safe control of organochlorine emissions. This work describes the process developed at IPEN/CNEN-SP (Nuclear and Energetic Research Institute/Brazilian Nuclear Energy Commission) for complete thermal decomposition of hazardous wastes through oxidation submerged in molten salts.

Key words: Pesticides, organochlorine, decomposition, molten, salt, oxidation.

1. Introduction

One of the largest problems that the modern societies have faced is the disposition of some industrial residues, particularly the hazardous and dangerous wastes. 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. Incinerators can release by the chimneys hazardous compounds, among which could be mentioned: heavy metals, organic material partially burned as PVC (Polyvinyl Chloride) or other PCIs (Incomplete Combustion Products), PAHs (Polycyclic Aromatic Hydrocarbons) [1].

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This study was motivated by the current interest in the world in the development of advanced processes for waste decomposition. This interest stems from the need for safer processes for the decomposition of some wastes, particularly those deemed hazardous or present significant impact on the environment. The technology developed fits into this principle and it is applicable for intrinsically safe disposal of hazardous organic wastes, particularly the organochlorides, whose degradation has presented problems when using the most common methods, such as incineration [2].

Pesticides banned, obsolete or discarded constitute a serious environmental risk around the world, especially in developing countries. Pesticides are among the compounds that constitute the group of so-called POPs, or persistent organic pollutants that are regulated internationally by the Basel Convention. Pesticides, dioxins and PCBs (Polychlorinated Biphenyls) are included among the major POPs. These compounds represent, according to the UNIDO (United Nations Industrial Development Organization), one of the most serious and urgent problems to be faced, due to their wide dissemination in environment and, secondly, because of their properties and characteristics, which determine its persistence in soil and water. The UNEP (United Nations Environmental Protection), for example, launched a global action for the establishment of an international treaty to reduce and/or eliminate emissions and discharges of 12 specific POPs, also known as “dirty dozen” (aldrin, chlordane, mirex, dieldrin, DDT (Dichlorodiphenyltrichloroethane), dioxins, furans, PCBs, endrin, heptachlor, toxaphene and BHC (Hexachlorocyclohexane)), besides the adoption of scientific criteria for the possible inclusion of others. The HCHs (Hexachlorcyclohexanes) also called BHC or lindane, are organochloride insecticides that have been banned in most countries in the 70s and 80s.

In this context, IPEN has developed the molten salt oxidation applicable mainly to the safe degradation of hazardous wastes. This study was motivated by the world interest in the development of advanced processes of waste decomposition, due to the need of safer decomposition processes, particularly for the POPs and the organochlorides, category in which most pesticides fit. A tendency observed at several countries is the adoption of progressively more demanding legislation for the atmospheric emissions, resultants of the waste decomposition processes. The suitable final disposal of hazardous organic wastes such as PCBs, pesticides, herbicides and hospital residues constitutes a serious problem. In some point of their lifecycles, these wastes should be destroyed, in reason of the risk that they represent for the human being, animals and plants.

2. Molten Salt Oxidation

The molten salt oxidation was initially developed in the fifties by the Rockwell International Co. for U.S. Atomic Energy Commission using molten fluorides. At first, the process was developed for activities of the nuclear fuel cycle not related to wastes decomposition. 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 [3-5]. 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 MSO (Molten Salt Oxidation) 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 [6].

In the molten salt oxidation, a molten alkaline salt as, for instance, Na_2CO_3 (Sodium Carbonate) 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 [4]. 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. Consequently, the process does not generate liquid wastes and this constitutes an important advantage.

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 1,000 °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. In the Fig. 1, it is presented a schematic drawing of the process developed at IPEN. In the Fig. 2, it can be seen a schematic drawing of the waste and air/oxygen injection lance, which plays a fundamental role in the process efficacy.

3. Pesticides Decomposition by Molten Salt Oxidation

Organochloride compounds can be decomposed in a safe way in the molten salt equipment because the chlorine present in the wastes reacts with elements present in the bath salt, such as sodium, for example, forming the sodium chloride which is retained in the salt. One objective of this study was to evaluate the threshold temperature at which the reactions of the chlorine present in pesticides still occur. It is important to mention that the retention of chlorine has

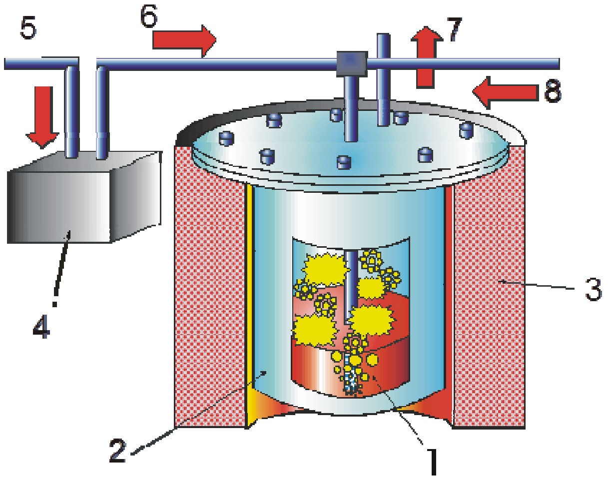

Fig. 1 Schematic drawing of the molten salt oxidation process where 1-molten salt, 2-reactor vessel, 3-heating system, 4-wastes pressurized reservoir, 5-compressed air, 6-waste feeding piping, 7-off gas, 8-air/oxygen injection.

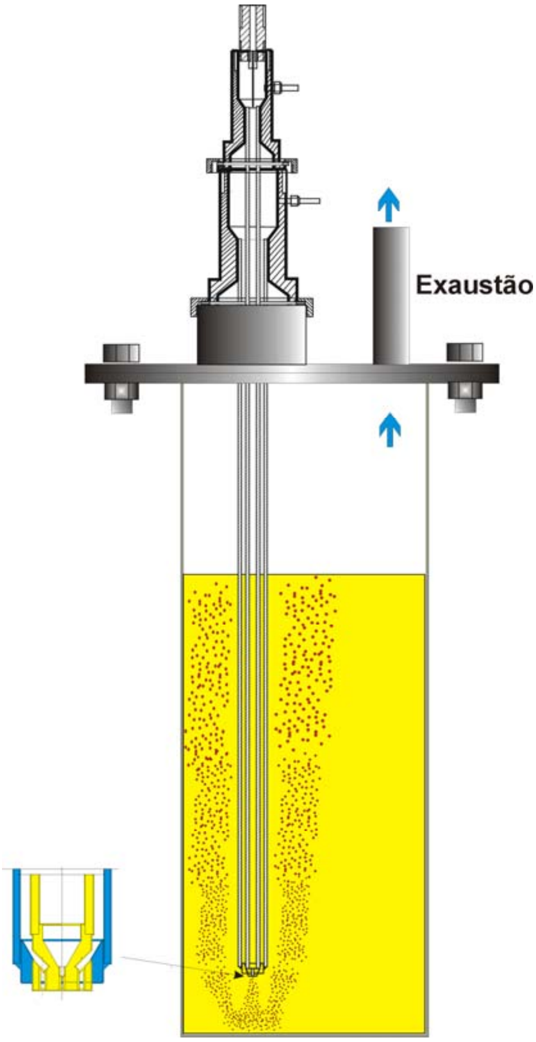

Fig. 2 Schematic drawing of the reaction vessel and the waste and air/oxygen injection lance.

greater importance than the oxidation of other constituents of organic waste, such as carbon and hydrogen. The saline bath which was being investigated consisted of pure sodium carbonate, whose melting temperature is 851 °C.

The first stage of this work was the selection of salt mixtures of low melting point. The activities involved will be described in detail in another paper at this conference. In the Table 1, the melting points of binary salt mixtures of different compositions (obtained experimentally) are presented. In the Table 2, the melting points of ternary salt mixtures are presented. It was chosen a mixture of carbonates of Li, Na and K with composition of 20A-60B-20C (mass ratio) respectively to decrease the melting temperature as much as possible. The salt mixtures constituted by sodium hydroxide and sodium carbonate presented unexpected corrosively for the equipment components and were not used in decomposition tests.

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.

Initially, in the first developments related to the technique adpted at IPEN, it was constructed a prototype

Table 1 Results of tests to determine experimentally the melting temperatures of binary salt mixtures preselected.

Salt mixture	Mass ratio of components A and B			
Na_2CO_3-NaOH	30A-70B	40A-60B	50A-50B	60A-40B
Melting temperature °C	238	254	264	318

Table 2 Results of tests to determine experimentally the melting temperatures of ternary salt mixtures preselected.

Salt mixture	Mass ratio of components A, B and C			
Li_2CO_3-Na_2CO_3-K_2CO_3	20A-40B-40C	20A-50B-30C	20A-60B-20C	20A-70B-10C
Melting temperature °C	452	412	402	492

with a small reactor vessel for preliminary evaluation tests, mainly with the objective of verifing the performance of construction materials in terms of corrosion reesistance [7, 8]. 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 environments in high temperatures.

In the next step, it was assembled a decomposition equipment constituted by two reactors, as can be observed in the Fig. 3. The waste (BHC in powder) was introduced with air in the first reactor and the gaseous products of the decomposition reactions in the first reactor were introduced in the second reactor with aditional supply of air. The salt composition was the same for both reactors, but the temperature of the first reactor was established in three different conditions: 450, 550 and 650 °C. The temperature of the second reactor was fixed in 650 °C. Two waste introduction rates were tested. Gas samples after the first reactor and after the second reactor were collected in each decomposition experiment and analyzed by gas chromatography and mass spectrometry coupled with gas chromatography. The gas chromatographer Shimadzu Model GC2010 has an ECD (Electron Capture Detector) suitable for chlorine compounds detection and a DB-5 column.

4. Results of the Decomposition Tests

The results have proved that chlorine can be retained at low temperatures, as mentioned above, by forming the corresponding chlorine salts, i.e. lithium, sodium and potassium chloride. These innocuous chlorides salts are retained in the molten salt bath.

It could be demonstrated that the decomposition of organochlorine compounds may be carried out at relatively low temperatures, i.e. of the order of 400 °C. The salt bath height was approximately 40 cm in both reactors and the introducing rate for BHC was established in a way that some BHC not decomposed could be observed in the gases releasing the first reactor. Two introducing rates were tested: 3.6 $kg \cdot h^{-1}$ and 7.2 $kg \cdot h^{-1}$. Analysis of the GC and GC/MS spectra of the first reactor effluents showed the presence of some BHC isomers not completely decomposed. Nevertheless, after leaving the second reactor, no BHC or molecular fragments containing halogens were found, in any condition, even in the most adverse condition, which demonstrates the effectiveness of the technique for decomposition of pesticides. The results for one set of experiments can be observed in the Fig. 4.

Fig. 3 Picture with the control panel and assembling in tandem of the two molten salt reactors.

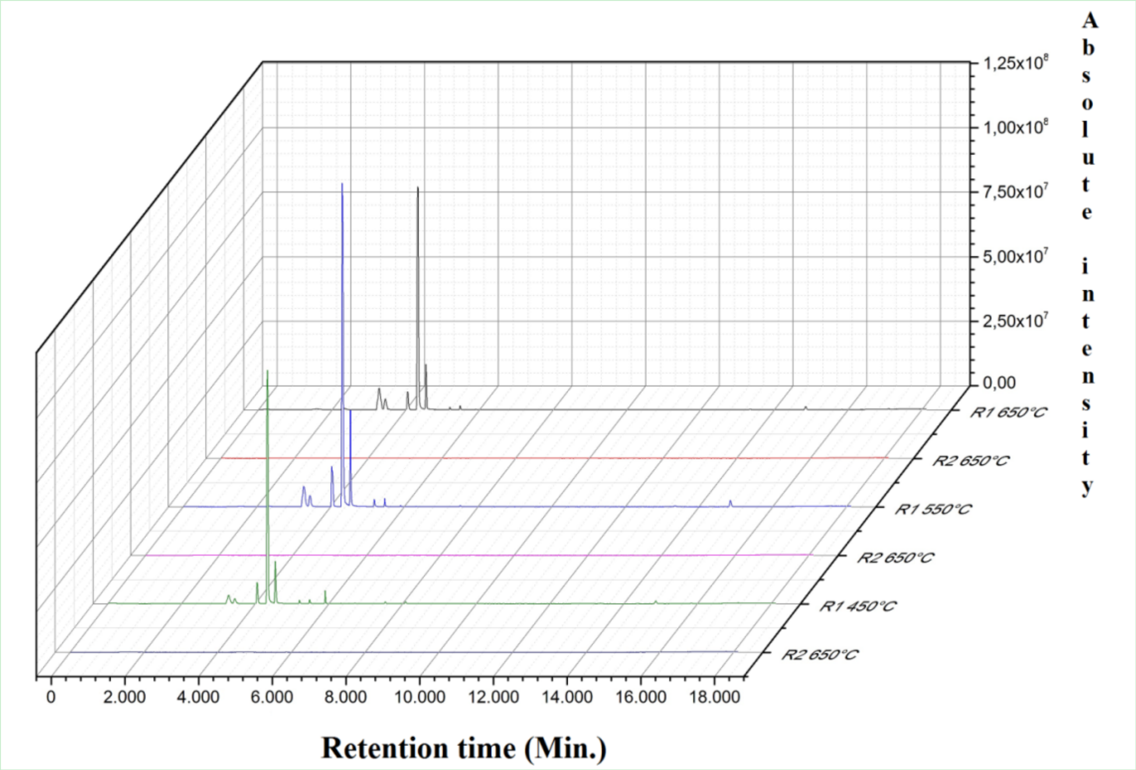

Fig. 4 Composition of the gaseous effluents from the decomposition of BHC by molten salt oxidation-analysis obtained by gas chromatography.

5. Conclusions

In the graphic presented in the Fig. 4, it can be observed that there are not products of the decomposition in the gases released in the second reactor—R2, for all temperature conditions. In a preliminary conclusion, it can be inferred that the residence time is more important than the temperature of the molten salts in the efficiency of the complete decomposition.

The molten salt oxidation is a process which promotes a more complete and safer decomposition of wastes considered critical, such as POPs, obsolete chemicals, extremely energetic compounds (propellants and explosives). Besides this, the main risk associated with the decomposition of organochlorides is the release of chlorine and its molecular recombination with hydrocarbons which may cause the formation of dioxins and furans. The formation of chlorine salts prevents the releasing of chlorine in the emissions and makes the process intrinsically safe.

It is important to emphasize that some nuclear spin-offs may have important contributions and provide benefits to different sectors of the society such as enlarge knowledge base, strengthen infrastructure and benefit technology development. Besides this, some useful technologies elapsed from nuclear activities, such as molten salt oxidation which can be used for safer decomposition of hazardous wastes also can affect favorably the public opinion about nuclear energy.

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