# Pyrolysis and

# High Performance Plasma Treatment

# applied for the treatment of

# Spent Ion Exchange Resins

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**Abstract**

Spent ion exchange resins (IERs) represent an important waste stream that is generated during the operation of nuclear power reactors and research facilities reactors. Over the past 70 years of nuclear activity, Argentina has accumulated near 400 m3 of spent IERs that remains storage for an adequate conditioning before disposal. An optimal processing option must involve volume reduction, production of a stable waste form and low radiological and environmental impact. Many technological options that fulfill these requirements were developed and applied in the nuclear industry worldwide, however, due to the size of the current inventory of our country is challenging to choose a favourable economic solution. In the last few years, our research group has been working on a novel two-step process involving initial low-temperature pyrolysis (< 350°C) of the IERs followed by a high performance plasma treatment (HPPT) of the produced off-gases. A bench scale arrangement that combines both technologies was assembled in our laboratory. The system works at sub atmospheric conditions and water steam is added to the gas stream as reagent. It has been observed that the presence of water in the medium results in the improvement of the properties of the solid product obtained, as well as participating as an oxidizing agent in plasma chemistry, contributing to the high performance of the off-gas treatment. The test results achieved using this arrangement were successful and demonstrate the feasibility of the proposed treatment concept. Also it is possible to take it to a reasonable scale implementation in a simple way, ensuring compliance of the requirements in terms of safety profile and minimum environmental and radiological impact. The present work will provide an overview of the overall process under development, paying particular attention to the obtained solid waste form characteristics and the efficiency of the off-gas treatment system.

## INTRODUCTION

Polymeric ion exchange resins (IERs) are key materials across a broad spectrum of industries [1], including the nuclear industry. Within nuclear power plants and research reactors, polystyrene divinylbenzene-based ion exchange resins are extensively employed in the cooling water systems to control chemistry quality.

The aim of these materials is to minimize corrosion or the degradation of system components and to remove radioactive species derived from activation and failed fuel elements. Once exhausted, however, these materials become one of the most important operational waste streams (in terms of volume) generated by the nuclear industry.

The treatment and conditioning of spent ion exchange resins is a complex process encompassing a detailed consideration of their physical and chemical characteristics and their compatibility with the management steps options. Basically, there are two main processing strategies: (a) the degradation of the organic materials with the objective of reducing the volume and producing an inorganic intermediate product, which may or may not be further conditioned, suitable for storage and disposal, and (b) direct immobilization in a matrix such as cement, bitumen or polymers [2]. Within the first group, a long list of processes have been developed including chemical [3], thermochemical [4], thermal, and biochemical ones [5].

Pyrolysis is one of the most attractive thermal methods and it is characterized as a low temperature flameless process (compared with high temperature thermal methods, e.g., incineration) in which the organic material is heated in a reducing atmosphere to leave a carbonaceous product or char. Being a flameless technology, pyrolysis has the advantage of lower operational temperature and, of critical importance in the nuclear context, an enhanced safety profile. Thus, pyrolysis features as an innovative technology in recent IAEA reports on thermal processing of radioactive wastes [6], being considered, and even practiced, as a method for the treatment and conditioning of radioactive organic wastes such as solvents, oils, and especially spent ion exchange resins derived from the operation of nuclear facilities.

In this field, the Pettersson and Kemmler’s [7] early experiences form the basis of subsequently developed industrial scale processes by companies such as Nukem [8] and Belgoprocess [9]. Another interesting example is the Thermal Organic Reduction (THORSM) process [10] carried out at the Erwin Resin Solutions Processing Facility (Energy Solutions, Inc., Salt Lake City, UT) in Erwin, TN, where approximately half of the spent resins generated by the U.S. power reactors have been treated. A major advantage of pyrolysis is the minimization of the dispersion risk present in high temperature processes (such as incineration, or direct plasma treatment) reducing by-product streams and also retaining a large part of radioactive inventory within the product. This simplifies the treatment of the off-gas stream since little or no radioactivity is expected to be present.

A very important issue to consider is that thermal decomposition of this kind of materials can lead to the formation of complex off-gas streams which are formed by compounds of diverse nature and toxicity, and should be processed in a safe and efficient way (generally through a post-combustion stage) in order to satisfy air emission regulations.

In the last few decades, plasma technology has emerged as a novel processing technology for environmental applications, such as the treatment of different waste streams, due to its high chemical reactivity [11]. This attribute combined with the possibility of having control of the reaction products and avoiding the emissions’ dilution, associated with the incorporation of additional fuels and air, positions plasma technology as a novel alternative for substitution of conventional high temperature processes at post-combustion systems for the elimination of diverse complex compounds, including the dioxins [12]. Also, this technology is widely applied in the nuclear industry for different purposes [13].

Argentina current spent IERs inventory is near 400 m3 and remains in storage for an adequate conditioning before disposal. In the last few years, many efforts have been made to develop a technological option that could fulfil technical requirements as well as being a favourable economic solution.

A novel two-step process involving initial low temperature pyrolysis of the IERs followed by a high performance plasma treatment (HPPT) of the produced off-gas stream has been under development.

Previous published work suggest that low temperature pyrolysis of spent resins allows to obtain an anhydrous and chemically stable carbonaceous solid product. The studies carried out with loaded resin beds indicated that at temperatures below 350°C the major part of the inventory is retained since volatility of most elements and leachability of many divalent cations were very low [14, 15]. The pyrolysis off-gas stream was also largely characterized and the evolution of many compounds of interest as function of process temperature was established [16].

Plasma chemistry studies were performed using model compounds. The results demonstrated the high destruction and removal efficiency that can be achieved with the used arrangement under a range of working conditions, at low reactor temperatures and with moderate power consumption [17].

A bench scale setup that combines both technologies has been assembled in our laboratory in order to analyse the performance of the conjunction of the processes. The present contribution will provide and discuss results related to assays carried out with the mentioned arrangement.

## mETHODOLOGY

The bench scale experimental setup (Fig. 1) consists of a pyrolytic treatment system coupled to cold plasma in flow gas treatment arrangement (HPPT). The plasma system works at low temperature and in sub-atmospheric conditions, using inductively coupled plasma operating at a frequency of 13.56 MHz.



*FIG. 1. Bench scale experimental setup used during the tests. System combines low temperature pyrolysis and high performance plasma treatment (HPPT). MFC: mass flow controllers, PT: pressure transducer.*

The pyrolytic treatment system is composed of a stainless steel reactor with cylindrical geometry. Both the reactor and the carrier gas inlet pipe were electrically heated. The resins were fed through a sealed system designed to work under sub-atmospheric conditions. The resins feed system consisted of a sealed cylindrical hopper, where the resins were loaded at the beginning of the operation, and a motorized screw. The mass flow rate of resins used during the tests was 35 g/h and would be possible to scale it to higher flow rates.

High purity argon and oxygen were used as carrier and plasma gases. The flow rate and composition of the gas streams were adjusted by a set of mass flow controllers (Horiba, SEC-Z500 series).

Steam is added to the system as reagent. The steam feed rate was controlled by injecting water, through a steam generator built using a sealed heating cartridge, with a peristaltic pump (Masterflex L/S Digital Drive, Cole Parmer). The water flow rate value used was 0.35 cm3/min.

The system was maintained under slight negative pressure by a chemically resistant vacuum pump (Vacuumbrand, PC 3004 VARIO).

The resins used throughout this study were nuclear grade cross-linked polystyrene divinylbenzene gel ion exchange mixed beds (MR3, Dowex) saturated in water and drained before treatment.

The argon flow rate at the pyrolysis reactor was 600 SCCM, while for the plasma reactor it was 500 SCCM. During some tests, a part of the argon incorporated in the plasma reactor was replaced by O2 (100 - 200 SCCM).

The temperature control, both in the pyrolysis reactor and in the plasma reactor, was carried out through type-J thermocouples. Plasma reactor temperatures were low with values between 60 and 100°C, while the pyrolysis reactor worked at a temperature of 350 ± 1°C.

The tests were carried out with a plasma power of 450 ± 10 W and an operating pressure of 50 mbar.

The gas sampling point was downstream of the pressure control system and the on-line characterization of the off-gas stream was performed once the system reached the steady-state. The samples were taken from a controlled temperature trap in order to maintain a stable water vapour pressure.

The concentration of some gases was determined by specific gas analysis equipment: Total Hydrocarbons (THC) and methane (APHA-370, Horiba) and Nitrogen Oxides (NOx), CO2 and CO (PG-250, Horiba). Standard gas mixtures and measurements made by the aforementioned devices were used as reference for direct gas analysis by mass spectrometry (Omnistar GSD320, Pfeiffer).

As a final conditioning stage, the gas stream was passed through a wet scrubber before being released to atmosphere.

## RESULTS AND DISCUSSION

In each test, approximately 40 g of mixed resin were treated, obtaining mass and volume reductions greater than 50%. These results fit within the expected range of reduction according to the observations in TGA analyses [15, 18, 19].

The incorporation of steam into the pyrolysis reactor allowed obtaining a solid product that did not form aggregates and is odourless. At the same time, the decomposition of the functional groups eliminates the electrostatic properties of the original material. These listed characteristics are of relevance, since they avoid the formation of undesirable incrustations in the reactor, as well as facilitate the transfer of the solid material after treatment.

The pyrolysed resins showed a very low water reabsorption capacity as seen in previous work [14]. This property of the material is of interest to prevent the resin from swelling, which can cause problems in a later possible immobilization stage, such as the decrease in compressive strength and the appearance of cracks.

The estimated mass values per kilogram of drained mixed bed resin of the main products obtained during process are listed in Table 1:

TABLE 1. ESTIMATED MASS OF PRODUCTS GENERATED FOR EACH KILOGRAM OF DRAINED MIXED BED RESINS TREATED BY PYROLYSIS AT 350°C IN Ar ATMOSPHERE

|  |  |
| --- | --- |
| Product | g/kg pyrolysed resin |
| Solid product | 464 |
| H2O | 349 |
| THC (\*) | 86.3 |
| Trimethylamine | 36.7 |
| SO2 | 21.7 |
| CO2 | 26.4 |
| CH4MethanolMethylamineOthers | 5.81.30.48.3 |

(\*) THC: Total Hydrocarbons (toluene, styrene, divinylbenzene, etc)

The main products derived from the rupture of functional groups are: trimethylamine (methylamine to a lesser extent) and SO2 [17, 19]. The amines are the forms in which nitrogen is emitted during the thermal process and contain the 99.9% of the mass of N present in the untreated resin. At the same time, SO2 is the major form in which sulfur is released, containing the 65% of the mass of S in the untreated resin. These values agree with literature [18].

These data suggest that the final solid product is composed mainly of carbon and, to a lesser extent, hydrogen and sulfur. The residual S participates in the formation of bonds that stabilize the matrix of the material [20].

The gas stream generated during the pyrolysis process was analysed. Fig. 2 shows the *m/z* signals associated with different compounds of interest present in the effluent treated by plasma and their behaviour with the incorporation of different molar fractions of O2 (***x*O2**) in the mixture during the tests.



*FIG. 2. Signal evolution of different compounds of interest as function of changes in molar fraction of O2 (m/z = 32) in medium. Base peak signals: H2 (m/z = 2), N2 (m/z = 28), CO2 (m/z = 44), NO2 (m/z = 46), N(CH3)3 (m/z = 58),*

*SO2 (m/z = 64) y C6H6 (m/z = 78). All signals were corrected by Ar signal (m/z = 40) in order to eliminate possible baseline fluctuations.*

The main products derived from the rupture of functional groups were monitored. The signal corresponding to trimethylamine (base peak *m/z* = 58) is below the detection limit. Also, under the applied operating conditions, the elimination of the hydrocarbons derived from the degradation of the organic matrix (toluene, styrene, etc.) was ensured even without the incorporation of O2. In the figure these compounds are represented by the C6H6 fragment (*m/z* = 78) which appears in the mass spectra of most aromatic organic compounds. These results are in accordance with the high performance of the designed cold plasma system to remove compounds of this nature (efficiency > 99.99% [16]).

The main carbon compound present in the treated stream is CO2, which together with SO2 are the major compounds. The fact that the oxidized species of C and S are present even for ***x*O2** = 0 is associated with the role of H2O in the reaction medium under plasma conditions as described in previous work [16].

Sulfur dioxide does not present any transformation in plasma under our working conditions and, due to its environmental implications, it cannot be emitted into atmosphere. Thus the removal in a later stage is needed, as conditioning of the resulting gas stream in the gas scrubber system.

The measurements show that N in the treated gas stream is mainly found as N2. Low values of NO2 concentration were registered and the incorporation of O2 to the medium caused a small increase (never exceeded 100 ppmv). These values are below the emission limits allowed for waste incineration plants present in international regulations [21]. This fact simplifies and economizes the subsequent conditioning gaseous effluent systems as DeNOx units could be dispensed.

The molar fraction of H2 (***x*H2**) in the final gas mixture shows values close to 0.02. This amount is consistent with data obtained in experiments with model molecules and is far from the region of flammability for H2 in reaction mixtures of comparable characteristics [17].

## CONCLUSIONS

The results obtained in the tests were successful and demonstrate the viability of the treatment concept.

The solid product obtained by the pyrolysis system is not reactive and has properties that make it compatible with various immobilization matrices, such as cement and polymeric resins. This ensures the possibility of obtaining a stable waste form adequate for storage and disposal.

The cold plasma system guarantee high efficiency in the removal of the organic compounds derived from the thermal degradation of the IERs present in the off-gas stream. The used operating conditions allowed having a good control over the reaction gas products, minimizing the production of H2 and the emission of NOx.

The combination of low temperature pyrolysis and high performance plasma treatment (HPPT) of the off-gas stream could be a novel solution for organic matrix nuclear wastes and could provide economic and safety advantages for countries with low and medium scale inventories.

The proposed system can be scaled up in a simple way, ensuring compliance of the requirements in terms of safety profile and minimum radiological and environmental impact.

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