



PREDIS

Milestone 46

Report on feasibility demonstration of the Wet oxidation and the Molten Salt oxidation routes for the treatment of RSOW: Description of the processes and basic physico-chemical properties of the reconditioned waste form

Date 28.06.2023 Version Final

Dissemination level: Public

Hélène Nonnet

CEA Marcoule

BP17171

30207 Bagnols/Cèze France

Helene.nonnet@cea.fr



This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.

Project acronym PREDIS	Project title PRE-DISposal management of radioactive waste	Grant agreement No. 945098
Milestone No. MS46	Milestone title Report on feasibility demonstration of the Wet oxidation and the Molten Salt oxidation routes for the treatment of RSOW: Description of the processes and basic physico-chemical properties of the reconditioned waste form	
WP No 6	Date version 28.06.2023	Due date M34
Lead beneficiary		
Main author Hélène Nonnet (CEA)	Reviewed by Thierry Mennecart, SCK CEN, WP6 Lead	Accepted by Maria Oksa, VTT, Coordinator
Contributing author(s) Jan Hadrava (CVRez), Josh Radford (USFD), Eros Mossini (POLIMI)		Pages 19

<p>Abstract</p> <p>This report summarises the description of the wet oxidation and the molten salt oxidation processes for the treatment of RSOW and the basic physico-chemical properties of the reconditioned waste form.</p> <p>Wet oxidation processes are developed at Polimi and USFD. Molten salt oxidation process is developed at CVRez.</p>
--

<p>Coordinator contact</p> <p>Maria Oksa VTT Technical Research Centre of Finland Ltd Kivimiehentie 3, Espoo / P.O. Box 1000, 02044 VTT, Finland E-mail: maria.oksa@vtt.fi Tel: +358 50 5365 844</p>
<p>Notification</p> <p>The use of the name of any authors or organization in advertising or publication in part of this report is only permissible with written authorisation from the VTT Technical Research Centre of Finland Ltd.</p>
<p>Acknowledgement</p> <p>This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.</p>

1 Wet Oxidation (University of Sheffield, USFD, UK)

Main author: Josh Radford

Contributing authors: Sam Walling, Claire Corkhill

At the University of Sheffield, we have trialled and optimised wet oxidation processing to treat ion exchange resins (Iron and copper catalysts, hydrogen peroxide, 90 – 100°C). The resulting residues were characterised to be a mixed iron-copper oxide. Further thermal treatment of the residues (HIP) will be conducted on simulant residues due to the low yield of the wet oxidation process and the sample requirements for the HIP process.

1.1 Wet Oxidation Process

USFD has been studying the use of Fenton wet oxidation to degrade and destroy organic ion exchange resins. At Sheffield this was achieved using H₂O₂, a suitable catalyst (here, a mixed copper and iron catalyst), and application of heat (90 – 100 °C). The resulting effluent after destruction of the resin was a cloudy suspension, from which many elements could be precipitated and filtered. This sludge was proposed for HIPing within WP 6.5, with a suitable quantity of this material, or a representative simulant material. The process produces strongly reactive hydroxyl & hydroperoxyl radicals to mineralise organics to CO₂ + H₂O through the following reactions:

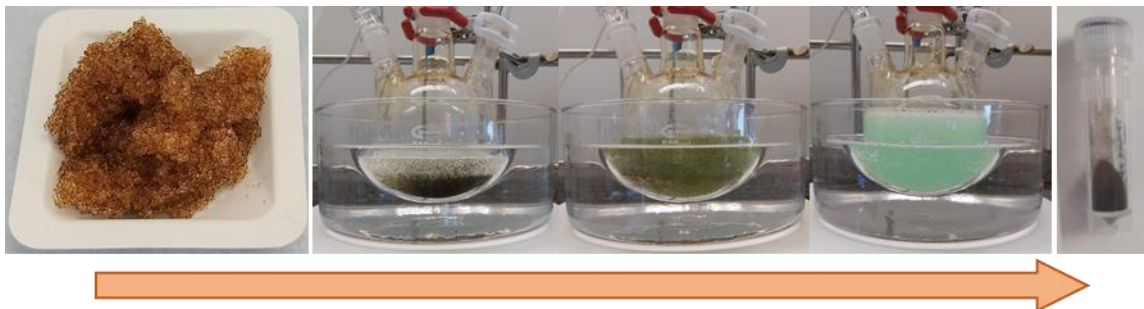
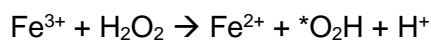


Figure 1: (from left to right) Amberlite ion exchange resin, various stages of the wet oxidation reaction, final product.

The wet oxidation rig at USFD is a small-scale fume hood based rig, in which a mixed cation:anion resin (Amberlite IRN-150) was treated, with >50 half-day runs to optimise processing conditions and suitably partition the effluent Figure 1. The optimised conditions utilised hydrogen peroxide and a mixed iron/copper sulfate catalyst at temperatures around 85 – 90 °C. Due to reactivity of the resin, and the size of the rig, only a small quantity of resin was treated per run (2.5 – 5 g). Very high level of mass reduction via destruction and oxidation to H₂O and CO₂ (~98% mass reduction after 3-4 hour processing), resulted in only small quantities of separated, dried sludge produced per run (<0.2 g). The resulting effluent after destruction of the resin was a cloudy suspension, from which many elements could be precipitated and filtered. Addition of alkali to the solution leads to the precipitation of wasteform, as can be seen in Figure 2.

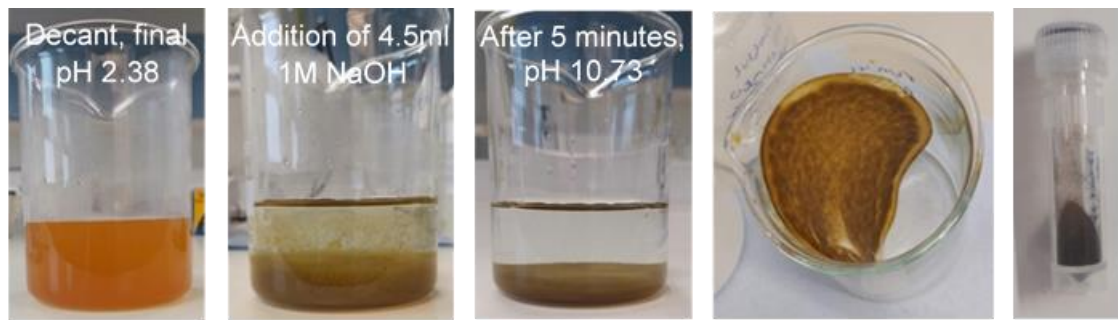


Figure 2: (from left to right) Final solution from the wet oxidation process, precipitation reaction following NaOH addition, settlement of precipitates, dried precipitate, final product

1.2 Characterisation of residues produced from wet oxidation process

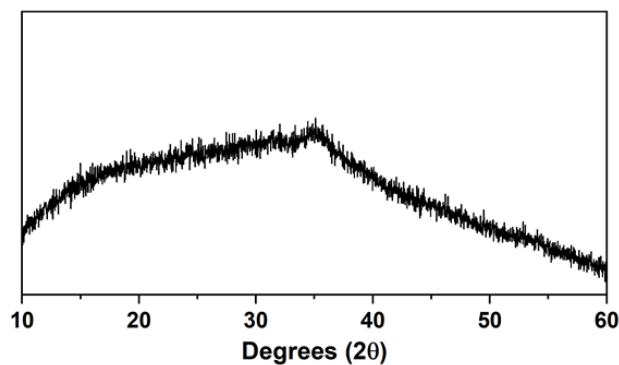


Figure 3: XRD pattern of precipitated, dried wet oxidation sludge

X-ray diffraction of the dried sludge (Figure 3) revealed a poorly crystalline iron/copper material, likely a disordered ferrihydrite material with sorbed copper, or with co-precipitated low crystallinity CuO. Chemical analysis of the sludge via energy dispersive x-ray spectroscopy (EDX) confirms this, in Table 1, along with some minor carbon and other impurities.

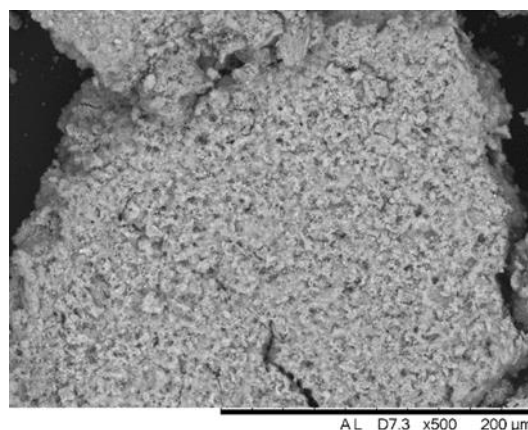


Figure 4: SEM image of dried powder

Table 1: Chemical composition of the sludge (EDX)

Component	Weight %
O	39.52 ± 4.92
Cu	22.81 ± 4.44
Fe	24.00 ± 2.31
C	8.50 ± 1.47
Al	2.55 ± 2.18
P	1.57 ± 0.22
S	0.98 ± 0.13

1.3 Simulant Materials to be used for immobilisation studies of wetox wastes

HIP processing will require substantial amounts of dried sludge. For other HIP trials within WP 6 (e.g. IRIS ash processing) an average of 18-19 g of material has been required. This would necessitate a very large amount of wet oxidation runs to produce enough material to HIP, and would be unfeasible for much larger-scale HIP runs, as planned by NNL within WP 6.5. Due to this, identification of a simulant material for HIP processing was required to permit a common material for processing between both small- and large-scale HIP trials.

For HIP processing, wetox material would be heated to 600°C as a ‘bake out’ procedure to drive off any free water or carbonate prior to sealing HIP cans. This pre-processing step was applied to combined wet oxidation material from multiple runs, to determine the final composition of the real material. Figure 5 shows the XRD pattern for the heated wetox material, revealing a crystallised mixture of Fe₂O₃ and CuO. These compounds are readily commercially available in large quantities to enable both small- and large-scale HIP trials.

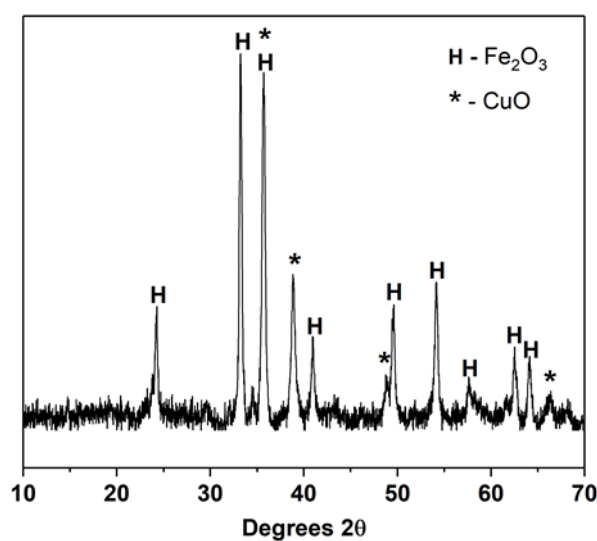


Figure 5: XRD pattern of heat treated powder

The crystalline composition of the baked out material, combined with the EDX chemical composition has allowed us to define a base simulant material as an equimolar 1:1 Fe:Cu mix of Fe_2O_3 and CuO . Further to this, a more complex simulant could be prepared with the addition of further oxides to represent co-precipitated radionuclides (e.g. Mn, Ni).

This base mix of Fe_2O_3 and CuO will be taken forward by USFD and NNL for HIP trials, to enable easy comparison between smaller and larger scale HIP cans. A mixture of these reagents has been prepared (~50g mixed from 1kg stocks of each reagent oxide, in June 2022), and already utilised for initial pre-HIP trials in WP 6.5 to determine suitable HIP processing temperatures. These initial trials have performed well, and has resulted in NNL purchasing quantities of the oxides to enable larger scale HIP trials to begin.

Overall, delivery of samples was completed, and a suitable simulant material was defined from laboratory reagents to enable comparable small-scale and large-scale HIP trials at USFD and NNL.

2 Fenton-like Wet Oxidation process (POLITECNICO di MILANO POLIMI, Italy)

Main author: F. Galluccio, E. Mossini

Contributing authors: A. Santi, G. Magugliani, E. Rizzi, M. Giola, E. Macerata, and M. Mariani

Fenton-like wet oxidation is a valuable and green strategy to cope with management of radioactive solid organic waste such as spent ion-exchange resins (IER). The self-sustaining process based on an exothermic reaction works at low temperatures ($< 100^{\circ}\text{C}$) by using cheap and green reagents. Indeed, this wet oxidative process can mitigate the energetic costs and the issue of off-gas streams (treatment of NO_x , SO_x , halogens), but also the risk of corrosion and the potential volatilization of radionuclides occurring in high-temperature thermal treatments.

Over the past 3 years, an experimental protocol was designed and implemented for the management of up to 200 g of resin, from the arrangement of the experimental set-up to the fine-tuning of the reagents in order to safely and efficiently control the oxidative process. Moreover, available and suitable techniques were deployed to characterize obtained liquors and solid residues before moving to encapsulation stage.

2.1 Process feasibility: progress to date

Based on a focused literature review and preliminary experimental evidence, the most important process parameters such as temperature, catalyst and oxidant amount, pH, and reaction time were fine-tuned to safely trigger and control the oxidative process. Furthermore, tuning of parameters was conducted to assure an optimal organic matter decomposition by limiting parasitic side-effects of the process. To date, POLIMI has effectively managed up to 200 g of cationic and mixed-bed resins by implementing a homogeneous wet oxidation in a four-necked round-bottom flask by using solutions of iron and copper sulphate salts as catalysts. The obtained liquors were characterized to assess the residual organic content by Total Organic Carbon (TOC) or Chemical Oxygen Demand (COD) and contaminants distribution by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). An evaporation process at controlled temperature (70°C) was conducted at the end of each oxidative process to obtain a final residue. To date, solid phases such as precipitates and post-evaporation residues have been preliminarily characterized by X-Ray Diffraction (XRD) analysis; however, presence of residual organic matter will be verified by using more appropriate techniques. Instead of encapsulating the final residue in cement matrix as performed in the past, POLIMI attempted a more sustainable and effective way by using a tuff-based geopolymer matrix, which should be more compatible with sulfur-rich residues. However, probable residual organic content and acidity of the residues posed some challenges in the encapsulation and made POLIMI explore heterogeneous wet oxidation. So far, a feasibility study with fly ash and electric arc blast furnace slag has been started to manage 10 g of undoped cation-exchange resin and have already provided some promising results. Finally, even though management of process off-gases is much less challenging compared to a conventional thermal treatment, it remains to be properly assessed. A schematic overview of the process tasks accomplished by POLIMI is depicted in Figure 6.

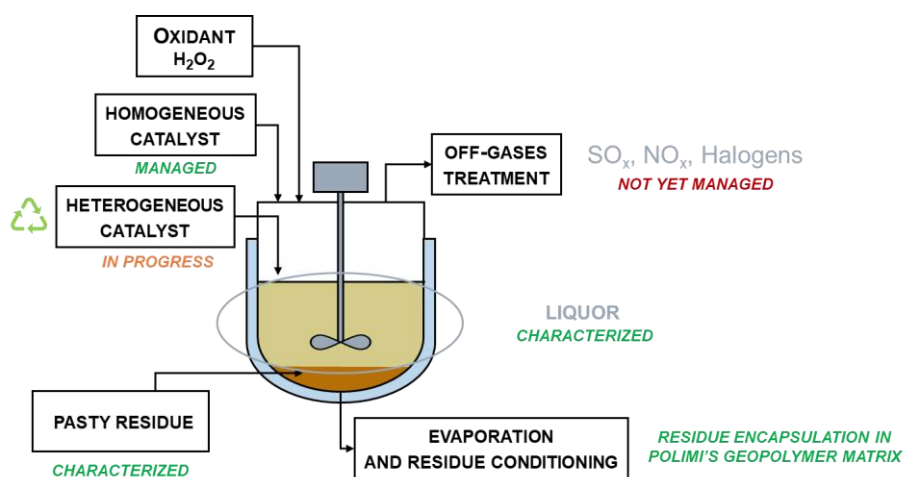


Figure 6: Schematic overview of wet oxidation process and tasks accomplished by POLIMI.

2.1.1 Design of a process protocol

Before running experiments, POLIMI developed a process protocol that encompasses from arrangement of experimental set-up to fine-tuning of the most relevant operating conditions thus triggering and controlling a wet oxidative process at small and intermediate laboratory scale. Depending on the size of the managed resin batch (from 10 g to 200 g), laboratory equipment and quantity of catalyst and oxidant were accordingly chosen and fine-tuned over time in accordance with a literature review and first experimental evidence.

2.1.2 Arrangement of an experimental set-up

POLIMI's laboratory is currently equipped with an experimental set-up appropriate for the management of 200 g of mixed-bed resin at most. Nevertheless, a chemical reactor is going to be integrated in the waste management environment of the laboratory thus accomplishing wet oxidation of organic matter at a larger scale. A quick overview of the experimental set-up used so far is given:

- Four-necked round-bottom flask as glass reactor (500 mL and 3000 mL) used for small (10g → 20 g) and intermediate (100 → 200 g) laboratory scale processes.
- Stirring heating mantle or thermal bath to control the reaction temperature and ensure proper mixing throughout the process.
- Glass thermometers to monitor the process temperature of the wet-ox mixture and off-gases over time.
- Peristaltic pump to ensure constant flow rate addition of the oxidant to the mixture of resin and the catalyst in the glass reactor.
- Condenser and receiving flask to condense released vapors.
- Bubblers filled with solutions (e.g., NaOH and H₂SO₄) may be used downstream of the glass reactor to trap CO₂ and other volatile species (e.g., iodine and chlorine).

2.1.3 Preparation of a surrogate waste

Instead of small and unloaded resin batches currently managed and reported in literature, POLIMI considered loading of larger cationic and mixed-bed resin with stable contaminants such as Cs, Sr, Co, Ni, Cl, I as representatives of fission and activation products to mockup a radioactive solid organic waste coming from a nuclear facility. Nuclear grade cationic (IRN 77) and anionic (IRN 78) resins were loaded by stock solutions of the stable contaminants. The achieved saturation factor with respect to ion exchangeable resin sites ranged from 10 % to 40 %.

2.1.4 The choice of catalysts

To date, POLIMI has conducted homogeneous wet oxidation process by using solutions of 0.2 M FeSO_4 for cationic resin, while 0.1 M FeSO_4 and 0.1 M CuSO_4 solutions were employed for a mixed-bed resin. On the other hand, the search for natural and industrial products such as fly ash and electric arc blast furnace slag is in progress to explore the more sustainable heterogeneous wet oxidation.

2.1.5 Cationic resin (10 g → 200 g)

After conducting trial runs with small batches of cationic resin to fine-tune and assess potentialities of the method, up to 100 g of doped cationic resin have been successfully treated. The process was triggered by the iron sulphates solution and dropwise addition of an oxidant (hydrogen peroxide). Within a few hours, the resin was decomposed, leaving a yellow solution and a fine precipitate at the bottom of the reactor.

The temperature profile showed a reaction peak at 90°C for about 1 hour, then it cooled down to about 75°C and remained constant for the rest of the process time. The color change of resin mixture was also used to track the evolution of the oxidative process. The mixture appeared black in correspondence with the peak at 90°C, then it shifted to brown and beyond yellow color as the organic matter progressively degraded. Beyond the visual inspection, the mineralization efficiency of cationic resin was assessed by measuring the TOC as a function of time. The highest value was found within 1 hour at the reaction peak, then it decreased consistently with temperature profile and color transitions (Table 2).

After evaporating the liquor, a reddish residue was obtained to be characterized and encapsulated. Elemental ICP-MS analysis was helpful to prove that no cation losses occurred. Scale-up of cationic resin management was successfully demonstrated up to 200 g of IERs. The process conducted at a different laboratory scale resulted in a mean weight reduction ratio of 63 ± 2 .

2.1.6 Mixed-bed resin (20 g → 200 g)

The oxidative process called for adjustments of oxidant and catalyst amount to treat a surrogate mixed-bed resin. In particular, the presence of the anionic resin needed a co-catalyst system (iron/copper sulphate solution) to achieve complete mineralization. Preliminary treatments were performed with 20 g of mixed-bed resin, where monitoring of temperature and color shift of resin mixture was helpful to understand the evolution of the process that resulted in a double-peak reaction because of longer degradation of the anionic IER. The reaction temperature showed a peak of about 90°C at early stage, while a second broad reaction peak at about 80°C was observed after 1 hour. Thereafter, the temperature decreased towards the mineralization of the mixed-bed resin. Consistently, the mixture turned dark at the first temperature peak, then hazel-colored and finally light yellow over 3 hours of oxidative process (Table 2). COD analysis demonstrated a gradual degradation of organic matter over time, while a whitish and fine residue was found at the bottom of the reactor. After treating a 20 g mixed-bed resin, a scale-up of the oxidative process was attempted for the management of at least 100 g of resins. The increased size of the batch involved the introduction of an external heat supply to safely trigger and control the oxidative process. At this scale, intense formation of bubbles and a double peak at 95°C occurred because of anionic resin decomposition, and this phenomenon became more pronounced when a 200 g mixed-bed resin was treated. Nevertheless, the efficacy of the process was promisingly controlled. At the end of the oxidation, more than 95 wt% of the initial Co, Ni and Cs was found in the resulting solution, while about 70% of the initial Sr was found in the precipitate. On the other hand, only a small amount (~10 wt%) of I and Cl remains in the final solution because the larger part of them came out as process off-gases and therefore must be suitably collected downstream of the glass reactor. The process

conducted at small and intermediate laboratory scale showed a mean weight reduction ratio of 79 ± 3 . However, the scale-up shifted the duration from 3 hours (20 g) to 15 hours (200 g), as reported in Table 2.

2.1.7 Characterization and encapsulation steps

The liquors from a cationic and mixed-bed resin oxidation were filtered to collect a small amount of fine residue precipitated at the bottom of the glass reactor. XRD identified the formation of strontium sulphate. After liquor evaporation, XRD investigations were conducted on the obtained residue and presence of mainly inorganic sulphate compounds was found. Besides strontium sulphate, iron sulphate [FeSO_4] was found in the case of the cationic resin. For the mixed-bed resin, the main species were the inorganic chalcantite [$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$], iron sulphate [FeSO_4] and, above all, ammonium copper sulphate hydrate [$(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$] and ammonium iron sulphate [$\text{NH}_4\text{Fe}(\text{SO}_4)_2$]. The residues coming from a mixed-bed resin wet oxidation underwent preliminary encapsulation into small equilateral cylindrical specimens (30 mm) at increasing waste loading factors 22, 28, 34, and 40 wt%. After proper time of curing, these trial specimens successfully hardened. Finally, XRD of the hardened specimens showed the presence of chabazite and sulphates as the main crystalline species, while a pronounced background suggests a significant fraction of an amorphous phase, partially attributable to the occurred geopolymerization.

Table 2: Fine-tuned operating parameters to manage a cationic and a mixed-bed resin by a homogeneous wet oxidation process.

Resin	Resin mass (g)	Catalyst volume (mL)	Oxidant flow rate (mL)	Liquor color transition	Process Time (h)	Evaporation Time (h)
Cationic	10	50	1	Orange → black → yellow	3	12 - 20
	100	500	2		5	
	200	500	2		8	
Mixed	20	50	1	Orange → dark brown → yellow	3	
	100	500	2		10	
	200	500	2		15	

2.2 Research Outlook

The management strategy achieved by a homogeneous Fenton-like wet oxidation calls for major efforts for the process optimization and implementation to a larger scale. To this purpose, POLIMI is going to equip its laboratory with a suitable chemical reactor to guarantee a complete mineralization of residual organic matter in the liquor and properly manage off-gases. Moreover, some of the drawbacks of homogeneous wet oxidation such as high amounts of sulphates and volumes of the final liquor, strong acidity of the sludge and poor durability of waste forms, could be overcome by exploring heterogeneous wet oxidation based on the use of recycled industrial by-products as potential catalysts, being at the same time precursors of the encapsulation matrix.

Acknowledgements

- This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.
- Collaborative Doctoral Partnership between Politecnico di Milano and European Commission's Joint Research Centre – Ispra site.
- Department of Earth Sciences at University of Milan for performing X-ray Diffraction spectroscopy.

3 Molten salt oxidation (CVRez, Czech Republic)

Main authors: J. Hadrava, V. Galek

Contributing author: Anna Sears

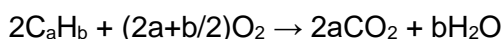
MSO (Molten Salt Oxidation) is a technology using the flame-free oxidation in molten salts materials in order to reduce the volume of hazardous solid and liquid wastes. Molten Salt Oxidation allows processing of the loose materials, semi-liquid suspensions or liquids over a wide range of viscosity. Combustible wastes are fed through the dosing system into the reactor together with air or oxygen. During the oxidation process, which is deliberately under the melt level, heavy metals and radionuclides are captured. This report deals with the process of combustion of an ion exchange resin containing stable Cs, Co and Sr isotopes. The research phase focuses on the dissipation of these isotopes in MSO technology within Task 6.3 for treatment of ion resins.

3.1.1 Molten salt oxidation process

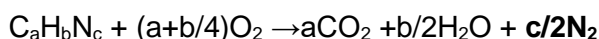
MSO is a thermal process designed for the disposal of organic waste. All organic carbon-containing wastes, together with excess combustion air, are conducted in the reaction vessel below the level of the salt melt, which has a temperature in the range 800-950°C. The melt is usually Na₂CO₃, K₂CO₃, Li₂CO₃, borates or other alkali salts or their eutectic mixtures.

At these temperatures, catalytic oxidation of the organic components to inorganic products such as CO, CO₂, H₂O, N₂ etc. occurs. The oxidation is followed by neutralization of acid gases containing halides and sulfur components in the melt. Molten salt has several functions. In the first case, molten salt serves as a dispersing medium for the treated waste and combustion air. The presence of salts accelerates the oxidation reactions, so that it also plays a role as a catalyst. Furthermore, the melt promotes a complete chemical reaction due to direct contact of the reactants and a stable heat exchanger that resists thermal shocks. The molten salts keep the soot and flue gases for completeness of the reactions and trap most of the ash, radionuclides, and other non-combustible waste components. Flameless oxidation products are discharged through the top of the reactor to the flue gas cleaning system. The gas must be free of coarse impurities including entrained salt and water vapor. Halogens and heteroatoms such as sulphur are converted to acid gases which react with the melt to form NaCl or Na₂SO₄. These are accumulated in molten salts according to the following reactions:

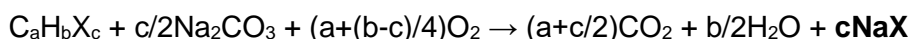
Oxidation process:



Nitrogen-containing wastes:



Wastes containing halogens (X):



One of the important factors for salt selection is the melting point of the molten salt. It is desirable that the melting point is low as possible to maintain the thermal stability at high temperatures. In addition, a lower salt temperature causes less corrosive load on the reactor vessel. One way to lower

the melting point is to combine multiple salts, called a eutectic mixture. These eutectic mixtures have a much lower melting point (400 °C) than the individual salt components and are characterized by a single melting point. After the dissociation of the salt in solution, both cations and anions can participate in electrochemical events associated with metal corrosion. Of the anions, chlorides have the greatest corrosion impact because they accelerate uniform corrosion and also cause crevice corrosion, point corrosion and corrosion cracking of stainless steels. The aggressiveness of bromides is comparable to that of chlorides. Iodides are less aggressive. Fluorides do not cause uneven forms of corrosion but accelerate even corrosion of stainless steels. Sulphide solutions cause the unalloyed steels to crack.

Austenitic chromium-nickel superalloys of the Hastelloy N type, Inconel 713 or pure nickel are resistant. In nitrates, even corrosion is very small, but at elevated temperatures corrosion cracking of unalloyed and low alloy steels can occur. Carbonates form solutions in which carbon steels are of limited use and chromium-nickel steels are resistant. At elevated temperatures, bicarbonates can cause corrosion cracking of carbon steels. Cations such as Fe^{3+} increase the oxidative capacity of the environment and have a negative effect on, for example, stainless steels in the presence of chlorides.

MSO has several advantages over combustion processes. The operating temperature of the process is lower than that of direct combustion and the radioactive substances are collected in the melt content. Alkaline melts interact with the acid components of the flue gas products, eliminating the need for tail gas purification. At the same time, the melt acts as a stable heat transfer medium that resists thermal shocks and provides thermal integrity.

Despite a few advantages, technology has its drawbacks. One of the main drawbacks is the lower economic advantage compared to the combustion processes since electric heating is used for operation. Another disadvantage is the lower lifetime of the construction materials in contact with the melt at high temperatures.

MSO technology in CV Řež consists of two reactors and operates in the temperature range from 400 to 950 °C. The temperature control in the reactors is separate and allows to set different temperatures in each reactor. The role of the second stage is often variable, but basically complements the first one and is mainly used for the high-temperature oxidation of flue gases with a high content of carbon monoxide, hydrocarbon residues and for the capture of fly ash containing radionuclides. In order to achieve an optimal oxidation, the temperature must be above 800 °C, and it is preferable to operate the reactor with at least 900 °C to reduce the necessary residence time of the reactants in the reactor.

MSO technology can also be operated in one stage. Several experiments were carried out in this arrangement. The change was that the molten salt was only in the first reactor. The second reactor without molten salt was passed through the flue gas from the first reactor directly to the portion following the gaseous products trapping aerosols and volatile metals. Some of the results measured on the laboratory apparatus were confirmed.

There are several independent processes taking place during the process, some of which have been identified during earlier laboratory tests and others occur when the equipment is expanded from laboratory to quarter operational. For example, after opening the gas outlet from the reactor, we notice on the flue gas analyzer that even without the intense flow of preheated air, the CO_2 gas moves. The source is thermolysis of alkali salts. The beginning is manifested by an increase in the amount of CO and CO_2 , when the oxygen content from the air is gradually reduced to zero.

The basic concept of MSO technology is shown in Figure 7.

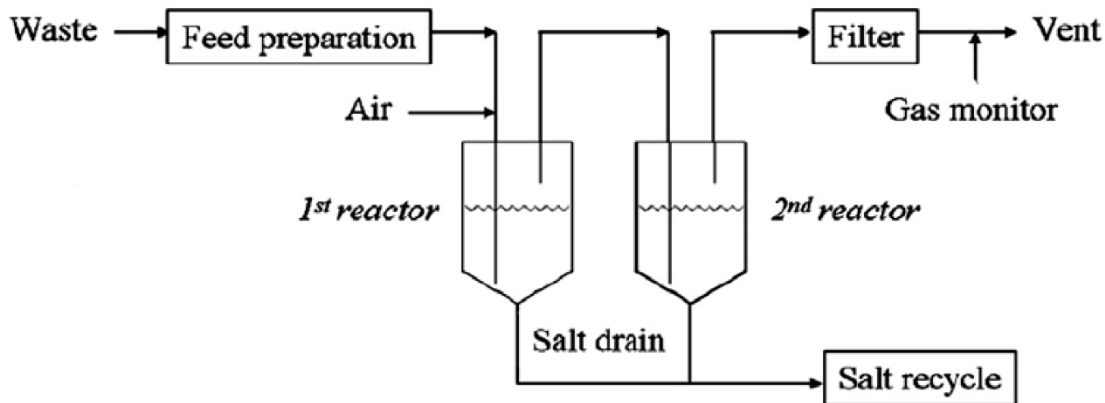


Figure 7: Schema of a two-stage system MSO

3.2 Process feasibility

3.2.1 Tested Ion exchangers

The real radioactive waste ion exchangers could not be used on MSO equipment and thus model contaminated ion exchangers were prepared. In principle, however, information on the chemical composition of the corresponding waste of nuclear power plants was used for their preparation, where ion exchangers serve as a purification element for waste water of the primary circuit.

The behavior of the used ion exchanger with simulated cation exchange activity PUROLITE C100-H and anion exchange PUROLITE A400MB-OH was studied. The amount of cesium, strontium and cobalt cations was determined for 1% wt. ion exchangers. The rest of the cation exchange capacity was saturated with Na^+ and K^+ ions and an anion exchange resin with BO_3^- and NO_3^- ions in a 1:1 molar ratio. Their consistency was sticky to plastic after partial dewatering and drying. In view of the anticipated but rather undesirable behavior of the adhesive materials in the dispensing device, further adjustments to the properties of the ion exchangers are desirable, in particular to reduce moisture. Drying was carried out at 65°C for 24 hours.

The results obtained with inactive modified contaminated ion exchangers, where the radioactive isotopes of waste ion exchangers were replaced in the same ratio by inactive isotopes, have replaced these tests from a physicochemical viewpoint of the whole process when verifying the technology. They were supplemented by other accompanying laboratory tests.

For the processing of waste ion exchangers by MSO technology, it is expected that especially well used ion exchangers will be available. Used ion exchangers with an adsorption capacity below the set limit become waste of variable properties at the nuclear power plant. They are used for systems in the primary circuit to treat feed water and refrigerant cleaning. It is significant how these materials behave under predictable conditions before they become waste. Significant are changes due to radiation or elevated temperatures, when the polymer part breaks down into even smaller organic particles, possibly even releasing H_2O and CO_2 . These transformations affect the chemical composition of the presumed waste to be reprocessed.

3.2.2 Oxidation medium

The oxidation medium for the MSO process may be air or oxygen. A defined ratio of oxygen to nitrogen from pressure vessels or air was used for combustion under laboratory conditions. Most of the tests in the past period on the MSO plant were conducted with air preheated to 400°C. Minimum air humidity was maintained by PSA column drying. The flow of oxidation medium was constant throughout the experiment.

3.2.3 Reactor vessel preparation and flue gas cleaning system

When filling the reactor with a defined salt, it is necessary to create a so-called cold stopper at the bottom of each reactor. Once formed, the salt is melted throughout the reactor volume. Sodium carbonate was used to prepare the melt. After the stopper has been formed in the first reactor and the melting of the salt has started, similar preparation work could be started in the second reactor (cold stopper and salt melting). Each reactor has a useful melting volume of about 70 dm³. Most tests are carried out with a weighing of 25 kg of salt, which approximately corresponds to 20 dm³ of molten salt during the process. Fuel (ion exchanger) is poured into the container for dosing the combusted solid component. It is possible to record the course of fuel dosing by the evaluation system because the tank is weighed by means of strain gauges. The weight change data is continuously read in the control system where it is interpreted. The temperatures of both reactors were set to 870°C. The mass flow rate of the ion exchanger was 0.5 kg/h. Oxidizing medium then with a flow rate of 25 m³/h. Secondary air for the second reactor with a flow rate of 6 m³/h. Total amount of incinerated waste 2kg per campaign.

The flue gases leaving the reactors, if properly optimized, should contain only CO₂, H₂O, and N₂. The apparatus is experimental and both unreacted gaseous substances and solid particles can be present in the flue gas. Thus the technology of the quarter operational MSO plant also includes a flue gas cleaning system consisting of a cyclone, two heat exchangers and a condensate separator. The last step is adsorption on activated carbon. Detectors for monitoring of outgoing gases are included. The output is condensate and emission gases.

Figure 8 shows the combustion over time, which occurs at certain intervals, both at the recorded oxygen consumption and at the formation of carbon dioxide. The shape of the intervals is influenced by the fuel feed rate and the oxygen supply from the air. At the same time, there is an impact of the capacity of the equipment. Similar intervals were also recorded when evaluating the process of the one-stage laboratory apparatus. This undesirable effect can be eliminated by increasing the dosing system and increasing the number of PSA columns.

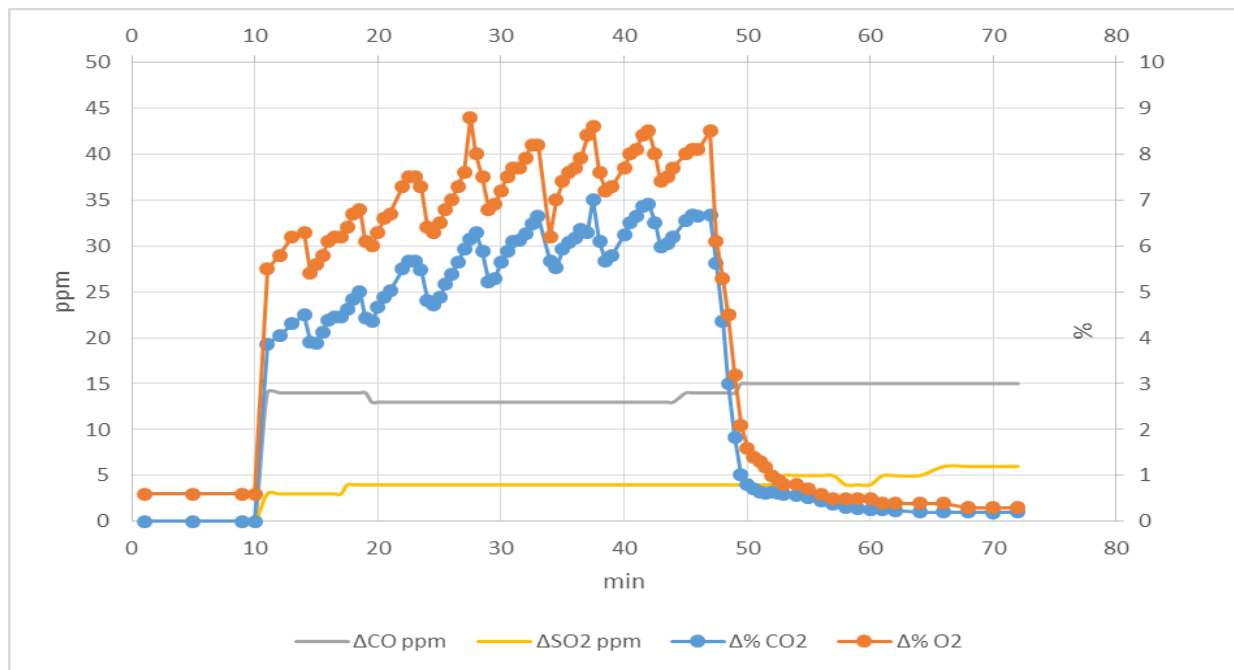


Figure 8: Two-stage MSO combustion: PUROLITE C100-H carbonated cation exchanger, 500 g charge, oxidation time 38 minutes.

3.2.4 Movement of monitored metals

Distribution of monitored metals in molten salt and in the flue gas cleaning system was monitored. A value of 0 is assigned to a detection limit of <math><0.020\text{ mg/l}</math> by chemical analysis (W-METMSFX). In particular, for cobalt, it is visible that it has been recorded at a lower concentration than the other metals. The explanation is that sampling was carried out by sampling from the molten discharged salt stream and the cobalt had accumulated in a portion between 25 to 50% of the level at the first reactor, as shown in Figure 9. It can be assumed that it may be below detection limit also in other samples. Another thing to consider is that cobalt is metallophilic and will more easily remain on the metal walls of the reactor.

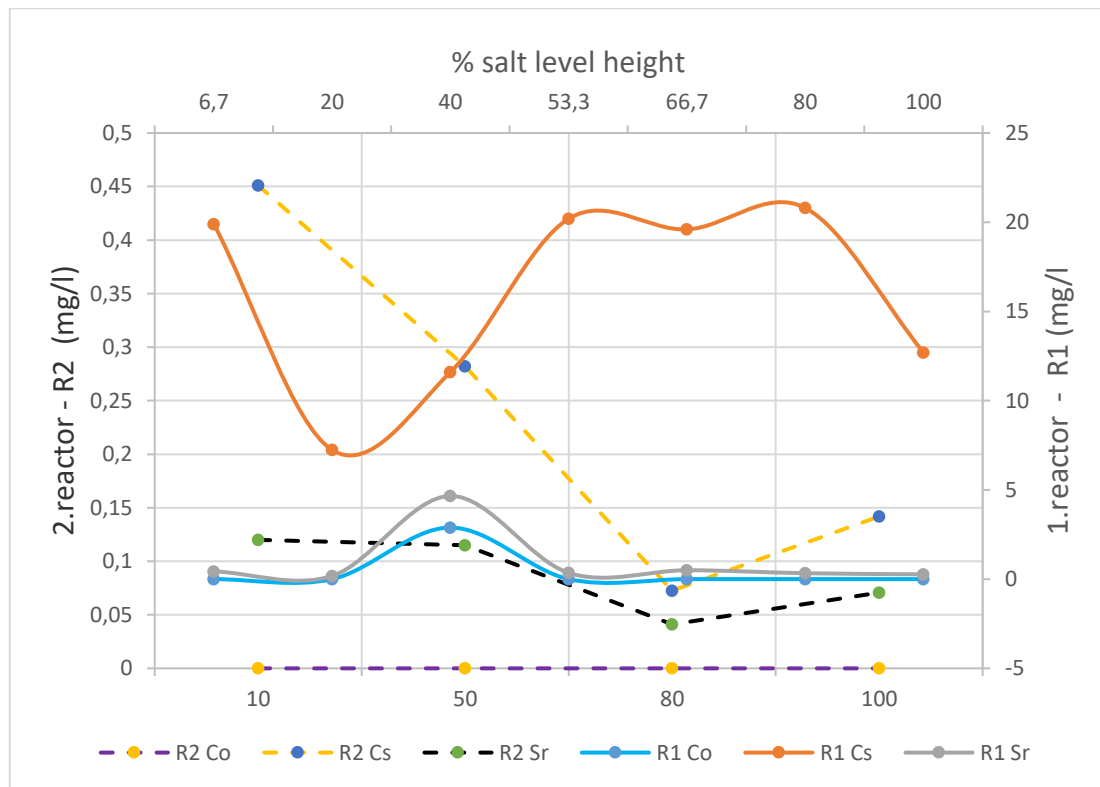


Figure 9: Distribution of metal concentration in the melt in reactor 1 and reactor 2 in the same experiment just prior to be discharged

From the point of view of experimental results, it is appropriate to compare the relative abundance of the monitored metals Co, Cs and Sr in the flue gas cleaning system, especially on two wire filters in series settling, see Table 3. Absolute amount depends on sampling method, way of reactor operating and settling time. Since the data were obtained by different methods, only the relative representation of metals among themselves can be compared quite well in this case. Since there was an equal weight percentage of each element in the material to be burned, it is clear from Table 3 that most Cs and significantly less of Co and least Sr are carried away by the flue gas.

Table 3: Leaking substances trapped on wire filters in the flue gas cleaning system - model carbonated cation exchanger containing Cs, Sr, Co

Element	Filter A		Filter B		Average relevant composition	
	mg	Measurement error	mg	Measurement error	mg	Measurement error
Na	0,606	0,02	0,382	0,02	0,494	0,02
Cs	0,087	0,01	0,068	0,008	0,0775	0,0085
Co	0,008	0	0,008	0,003	0,008	0,003
Sr	0,003	0	0,005	0,002	0,004	0,002
Si	0,022	0	0,128	0,01	0,075	0,007
Cl	0,017	0	0,02	0,004	0,0185	0,004
Ca	0,01	0	0,015	0,004	0,0125	0,0035
Ti	0,009	0	0,013	0,003	0,011	0,003
Al	0,008	0	0,01	0,003	0,009	0,003
Fe	0,003	0	0,004	0,002	0,0035	0,002
Zn	0,002	0	0,002	0,001	0,002	0,001
P	0,001	0	0,001	0,001	0,001	0,001
Cu	0,001	0				
Br			0,002	0,001		
Mg			0,006	0,002		

3.3 Research Outlook

Tests were carried out with simulated composition of inactive model ion exchangers in carbonate and borate melts and knowledge of real degraded ion exchangers was obtained. Quarter operating of the MSO process technology in borate melts is considerably disadvantageous for a given temperature range, and therefore melting in carbonate melts have been done. Protocol verification of the technology was carried out in a sodium carbonate melt with high oxidation efficiency. Waste gas products, heavy metals and stable isotopes were monitored in experiments.

Among other things, waste salt was used to cooperate in task T.6.4 as a filler in the geopolymer matrix.

The possible use of the molten salt can be divided into groups 1) general waste disposal, 2) specific treatment of wastes from specific facilities and 3) recovery as treatment facilities for other materials.

Materials that can be considered as fuel can be processed, both in solid phase in defined grain size and in liquid substances defined in viscosity from 1 – 10 000 mPas.

The general waste disposal concerns mainly perchloroethylene, hexachlorobenzene, polychlorinated biphenyls (PCBs) and the disposal of mixed wastes with hazardous and radioactive properties, as well as the destruction of explosives and other hazardous substances (PCE, TCE).

Specific treatment of wastes from specific plants mainly concerns outputs from nuclear power plants (degraded sorbents, ion exchangers, oils, decontamination solutions and cleaning materials, scintillation solutions, air conditioning filters), fusion power plant (tritiated waste and dust, filters, decontamination solutions and cleaning materials), from chemical plants (radiopharmaceuticals, heavy metals).

When using the MSO technology in combination with other technologies it will be very sophisticated equipment (fractionation of specific isotopes of elements including construction materials, various types of recycling and concentration of specific materials).

Acknowledgements

This project has received funding from the Euratom research and training programme 2019-2020 under grant agreement No 945098.