Methods of advanced waste conditioning by microwave internal gelation: Set-up development and modelling

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Abstract

Based on closed packed microspheres produced by gelation, Sphere-pac is a promising concept for the transmutation of minor actinides in fast reactors [1]. In the case of internal gelation, the chemical reaction is triggered by a temperature increase within aqueous droplets. Since microwaves provide a fast and volumetric heating, a set-up is developed in PSI where the microspheres undergo gelation as they cross the electromagnetic field generated inside a cavity [2].

This work presents the current set-up of the particle production unit. The components have been selected and mounted in such a way that the production can be remotely operated. An automation programme is being developed in order to optimise the critical parameters during operation. This will allow a safe and easy control of the equipment when the cavity is placed in a glovebox with radioactive materials.

The described unit has been used to heat water and cerium solution droplets, the latter being considered as a surrogate for active materials. The obtained results are reported and discussed here. To support the experimental data, a modelling of the electromagnetic field generated in the cavity has been developed. The perturbation of the field caused by the presence of a droplet and the amount of absorbed energy can be simulated. These experimental and theoretical studies enable the optimisation of the microwave cavity design and the determination of the needed power for the production of fuel microspheres.

Introduction

Sphere-pac fuel is a particle fuel which derives from a wet reprocessing route. The nitrate solutions containing the dissolved and separated spent fuel serve as an educt of the internal gelation process, which will be described in greater detail later. The gelation serves as a solidification process to produce small spheres (in the size range from 50 µm to 1 mm), which, after thermal treatment, are filled into the cladding, replacing the classical pellet fuel. The motivation in developing an alternative route to the classical pellet process lies in the simplicity and cleanness of the process, making it favourable in a remote operation mode, as it becomes necessary due to the high activity of the dissolved spent fuel. This process enables the fabrication of fuel enriched with minor actinides which can be burnt in a fast reactor, thus decreasing the radiotoxicity of spent fuel [1]. An alternative approach is the Vibropack concept coming from dry reprocessing. Both of these concepts are described in detail in [2], also including experimental results of irradiation programmes.

The internal gelation process and the Sphere-pac concept were extensively studied at PSI producing nitride, carbide and oxide fuels [3]. The internal gelation is triggered by a temperature shift, which was in the past realised by immersion into a hot silicon bath, involving a sophisticated cleaning process of gelled spheres. In two new programmes, the PINE [4] and MeAWaT [5] projects funded by the "Competence Center Energy and Mobility" (ccem.ch), an alternative approach is studied, where the temperature shift is realised by exposure to a microwave (MW) field [6]. This paper describes the implementation as well as some theoretical considerations of the so-called microwave internal gelation process.

Presentation of the gelation unit

Because the production unit is in its developmental phase, cerium was chosen as a surrogate for the actinide components of the envisaged fuel [7]. The broth used in the process is a mixture of a metal solution made with cerium nitrate $Ce(NH_4)_2(NO_3)_6$ purum, Sigma-Aldrich) dissolved in water and another solution (later called hexa solution) made with hexamethylenetetramine [also called HMTA, $(CH_2)_6N_4$] and urea (NH_2CONH_2) also dissolved in water. Both solutions have to be cooled down to 0°C, so that upon mixture the urea will complex with the cerium ions [8] and prevent a premature gelation. Upon heating, a series of chemical reactions occur in the broth (Figure 1); the urea will decomplex the metal ion as the HMTA undergoes a protonation (Equation 1) and decompose while consuming H^+ ions (Equation 2), thus increasing the pH in the solution and triggering the precipitation of the metal [9]. This last step corresponds to gelation. A further increase of the pH is also driven by the comsumption of one of HMTA's thermal decomposition products, formaldehyde (CH_2O) by urea [10].

Equation 1: $$((CH_2)_6N_4)_{aq} + H^+ \longrightarrow [(CH_2)_6N_4H]^+$$

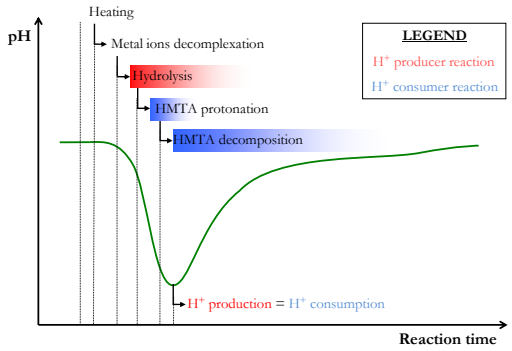
Equation 2: $$[(CH_2)_6N_4H]^+ + 3H^+ + 6H_2O \xrightarrow{T\uparrow} 4NH_4^+ + 6CH_2O$$

In contrast with the usual internal gelation process where the drop of broth is heated by contact with hot oil [12], a set-up at PSI has been developed where the drop temperature is increased by microwave heating in the X band (8 to 12 GHz). This rids the production unit of a cleaning step for the fuel spheres (contaminated with oil) and a recycling step for the oil.

Although internal gelation is not new in the nuclear industry (the KEMA process goes back to 1970 [13]), PSI innovates by developing a unit for microwave assisted internal gelation. According to their function in the production process, the components can be

regrouped in 3 points: the broth preparation, the liquid drop generation and the microwave equipment.

Figure 1: Schematic evolution of the chemical reactions occurring upon heating of the broth



Graph adapted from Collins [11].

Broth preparation

As explained in the previous section, the gelation occurs when the broth reaches a given pH. The sensitivity with which the broth will gel thus depends on the initial pH of the broth and the potential for a temperature induced pH shift (i.e. the amount of HMTA). The initial pH of the broth is determined by the amount of base (NaOH in the current work) mixed with the metal nitrate solution. The magnitude of the temperature induced pH shift is obtained by controlling the concentration ratio between the HMTA and the metal nitrate. Because of its premature gelation preventing role (that is, before heating), the urea concentration is critical when mixing the solutions. Characterisation of the internal gelation advancement and final state has been described in other works [9] [14] [15]. Since a maximum amount of metal is washed in the broth and because the gelled spheres should be as dry as possible after gelation, the lowest possible amount of water is used. Therefore, the solutions are saturated with the salts, 54.83 g of Ce (IV) nitrate is currently used for the preparation of 195 ml of broth. The urea/HMTA, hexa solution/metal solution and base/metal concentration ratios are 1.0, 3.0 and 0.2, respectively. The recommended values are in the same order of magnitude as those of Collin's study [9], although in the case of the microwave heating less time is given to the gelation.

Drop generation

The broth is filled into a cooled tank with a stirring device. Thanks to pressurised air, the broth is pushed towards a nozzle with a given diameter, which is chosen according to the targeted final drop diameter. The sessile drop forming at the nozzle falls by gravitation. Optical sensors are placed on the top of the cavity and deliver a signal when a drop is detected. In order to avoid premature gelation, the temperature of the broth from the tank to the nozzle has to be controlled. Therefore, double wall tank and feeding pipe are used, which are connected to a cooling unit. The temperature of the coolant is set to 5°C. Although this work focuses on the generation of large droplets, smaller spheres can be produced in order to obtain a high fuel density in the Sphere Pac concept [16] with only slight changes, such as a higher air pressure and the use of a vibrator. Details of small droplet production will be communicated in a separate work. In all cases,

due to their small sizes (2 mm maximum) and the high surface tension, the drops have a spherical shape.

Microwave equipment

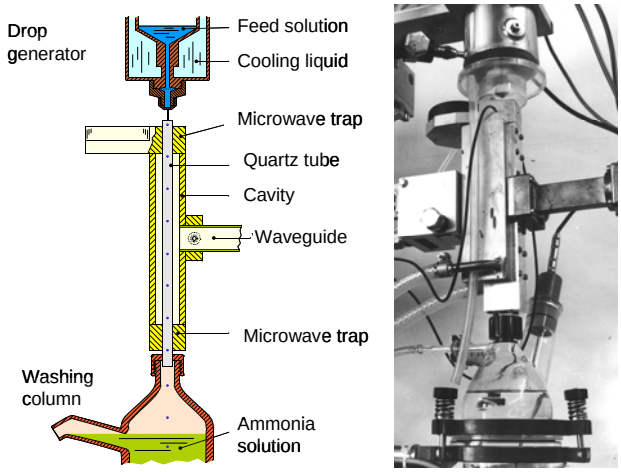
Once a drop has left the nozzle, it falls through a resonant microwave cavity aligned vertically. Inside the cavity, the drop absorbs energy from the interaction with the electric field generated inside it. The E-field is obtained with an X-band frequency generator working at 11.074 GHz coupled with an amplifier which works up to 250 W. When the drops exit the cavity they are already transformed into gel spheres and collected in a bath (see Figure 2).

A circulator is used to protect the amplifier from any signal coming back from the cavity, and a termination is installed to dissipate the reflected signal. A directional coupler is connected from the cavity to an oscilloscope through a Schottky diode. Therefore, the absorbed power during the drop fall in the cavity can be measured. During the residence time of the drop in the cavity (typically 120 ms), the amount of absorbed energy must be sufficient to heat the drop up to 60°C, the minimal working temperature for internal gelation to occur before the drop reaches the bath. Meanwhile, the MW power can also not be too high in order to avoid an overheating of the drop, leading to its explosion by inner vapour pressure. In order to protect the cavity from any contamination by the drops, a quartz tube is placed inside. The target temperature of the drops for the best results is set at 80°C. The heat generation rate Q_{gen} (W m^{-3}) applied to the drops is given by the following equation:

Equation 3:
$$Q_{gen} = 2\pi f_0 \varepsilon_0 \varepsilon'' E_{RMS}$$

where ε_0 and ε'' and E_{RMS} are the vacuum permittivity, loss factor and root mean square of the electric field, respectively, and f_0 (Hz) is the resonant frequency obtained with the dimensions of the design cavity for a given microwave mode. A high resonant frequency is used for a better heating efficiency. Because the walls of the cavity absorb a part of the MW energy, its temperature increases, inducing a slight change in geometry and consequently a shift in the resonant properties. In order to prevent this effect, a coolant also flows in the cavity walls.

Figure 2: Schematic view and photo of the set-up near the microwave resonant cavity



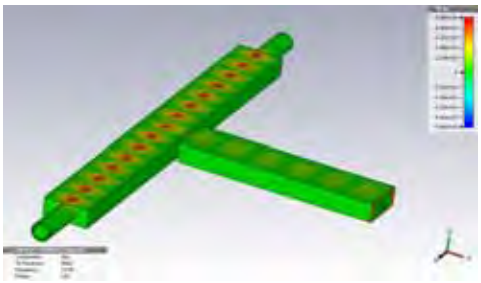
Microwave heating

Microwave heating is convenient for sphere pac fuel production because it is fast and volumetric. This technique is, however, sensitive and its efficiency drastically decreases when operating parameters are not optimised. Although satisfying heating conditions can be experimentally determined, the understanding of the electromagnetic field with the water molecules is crucial. In this section both simulated and experimental heating results are presented.

Modelling the resonant cavity

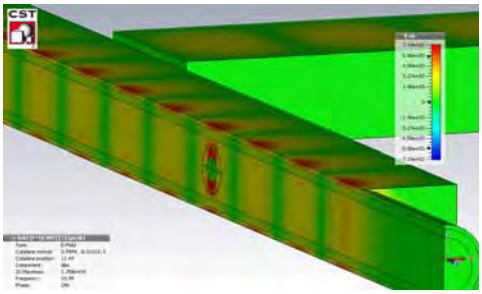
In order to understand how the power is dissipated inside the drop, a model of the cavity has been implemented with CST Microwave Studio [17]. The distribution of the field is first simulated in an empty cavity, and then a drop of water is inserted. First, the cavity heating in the TE_{1015} mode was modelled (Figure 3) and the magnitude of the E-field distribution was generated along the cavity at 11.074 GHz calculated. The signal is coupled through an iris from an X-band waveguide. The model includes a quartz tube as in the experimental set-up. The typical field distribution of the transverse mode is observed.

Figure 3: CST- MWS simulation of the magnitude of the E-field distribution in a TE_{1015} microwave rectangular cavity at 11.074 GHz



In another simulation, a water drop is placed inside the cavity at a fixed position (at a maximum of the E-field). When plotted with a cut along the x axis through the half x-dimension of the rectangular cavity (Figure 4), it is possible to observe how the drop disturbs the E-field while absorbing the microwave energy, thus increases its temperature. A virtual sphere and planes are drawn surrounding and splitting the drop for a better appreciation of its interaction with the field.

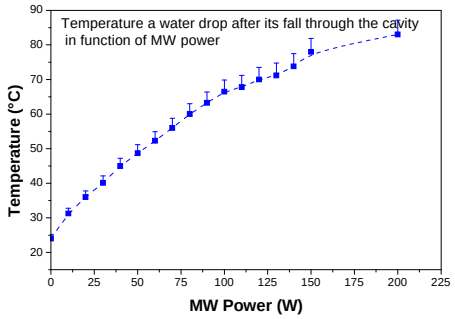
Figure 4: CST- MWS simulation of the magnitude of the E-field distribution, local perturbation of the electric field



Obtained results

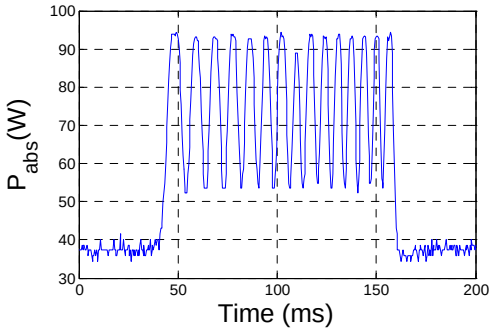
In order to complement the simulation, a drop temperature measurement was carried out on heated water drops, as shown in Figure 5. The uncertainty is a result of the measurement method: the drop is collected 20 cm below the cavity in a cup made of insulating material, at the bottom of which a thermocouple is placed. The drops were generated at room temperatures for this experiment. The drops are hotter with higher MW power. A decrease in the heating efficiency can be seen: this is mainly due to the lack of cavity cooling for this experiment which affects its geometry. It is still, however, possible to reach gelation temperature with about 200 Watt.

Figure 5: Measured temperature of a 2 mm diameter water drop after its fall through the heating cavity



From the signal recovered through the oscilloscope it is possible to read the absorbed power during the residence time of one drop inside the cavity. Figure 6 shows the absorbed power by a drop and the walls of the cavity during the gelation process of cerium solution drops, for an input power of 150 W, working with the TE_{1015} mode at a resonant frequency of 11.046 GHz. Although the power absorbed by the drop can not be differentiated from that of the walls of the cavity, it appears that the drop undergoes alternative heating.

Figure 6: Absorbed power during the gelation process for P_{in}=150 W



When microspheres from a cerium solution are fabricated, they are collected in a metal basket placed in a beaker. The beaker is filled with water in order to reduce the impact of the soft spheres. Figure 7 shows a picture of gelled spheres, before they are dried, aged in ammonia or thermally treated. The average size of a drop is 2 mm diameter.

Figure 7: Photograph of the gelled spheres (collected after gelation)

Developments foreseen for actinide handling

Although the current tests are carried out with an inactive surrogate, the equipment is chosen and installed in a way as close as possible to the final production unit where actinides will be handled. To prevent contamination of the environment, all the instruments directly in contact with the broth have to be placed in a sealed environment; therefore, the transfer of the production unit into a glovebox is being studied and this section gives an overview of the challenges to overcome when working with radioactive elements.

Transfer to a glovebox

Since the part being transferred into the glovebox is going to be contaminated and is subject to later active disposal, it will be minimised. Also, maintenance is much longer and more difficult when the device is inside the glovebox.

The cooling unit will remain outside the glovebox and a primary circuit connected by a heat exchanger will be run by a pump and installed in the glovebox. Concerning the microwave equipment, only the cavity and one waveguide will be placed in the glovebox. All the other components remain well accessible and inactive outside of the box. A sapphire window or coaxial connectors will be placed on a wall that will let the microwave enter the glovebox. The effect of this transmission window must be minimal as far as the safety and heating efficiency are concerned. The nozzle on the top of the cavity and the bath at its bottom ensure that no metallic component can enter the cavity holes and thus prevent the risk of sparks and shortcuts. Regarding the contamination inside the glovebox, the transient state when the first drops of broth are generated is delicate since drops occasionally fall with a horizontal speed component. Retrievable inserts have to be developed to protect the rest of the equipment.

When an experiment is finished, some gelled solution sticks to the walls of the broth pipe. To clean it, the nozzle must be closed and the pipe filled with a liquid, where an ultrasonic finger will be sunk. Because the liquid is then purged, ethanol is selected for its high volatility; it can then be disposed on a plate and left for evaporation. The dry subtracts can be later collected from the plate.

Remote operation

To enhance the safety of the operator, the operations should be remotely performed. To do so, all the mechanic, electronic and electric components are chosen so that they can be centrally controlled from a computer. A computer interface tool (i.e. Labview) is foreseen to turn on/off the unit and tune each parameter separately. In a more distant future, an optimisation routine can be used to follow up the reflected signal from the

cavity and find the best heating parameters. This can only be achieved with a very high speed communication device since a frequency sweep has to be performed.

Decay of the minor actinides

Because of the high activity of the MA (minor actinides) compared to cerium (or uranium), two critical aspects have to be taken into account when producing microspheres with internal gelation. The first aspect is the decay heat, which could be a cause for premature gelation. Table 1 reports the decay heat and the concentration of the respective minor actinides in a SFR fuel (example of TRU fuel composition taken from [18], which does not include ^{242}Cm with a decay heat of 122 W/g) and a calculated estimation of the decay heat contribution per actinide in the broth. Even when mixed with the hexa/urea solution, the decay heat is not neglectable. The calculated 2.56 Watt per liter is in the same range as the few tens of Watt per kg of heavy metal calculated by Kawaguchi [19]. To avoid this, a suitable cooling unit must be used and the section of the tank and feeding pipe should be minimised. The other aspect is radiolysis, which forms hydrogen (water radiolysis) and can even decompose gelation reactants (i.e. urea and HMTA). A solution is considered where the mixture of the two solutions is performed right before the generation of the drop.

Table 1: Half life and decay heat of ^{238}U and of MA in SFR fuel

Isotope	Half-life (years)	Decay heat (W/g)	Concentration in broth (g/l)	Decay heat in broth due to isotope (W/l)
^{237}Np	2.1×10^{6}	2.0×10^{-5}	1.66	3.32×10^{-5}
^{238}Pu	8.8×10^{2}	5.6×10^{-1}	1.88	1.07
^{239}Pu	2.4×10^{4}	2×10^{-3}	1.27×10^{1}	2.54×10^{-2}
^{240}Pu	6.5×10^{3}	7.0×10^{-3}	6.59	4.62×10^{-2}
^{241}Pu	1.4×10^{1}	3.0×10^{-3}	7.06×10^{-1}	2.12×10^{-3}
^{242}Pu	3.87×10^{5}	1.0×10^{-4}	1.65	1.65×10^{-4}
^{241}Am	4.3×10^{3}	1.1×10^{-1}	3.16	3.63×10^{-1}
^{242m}Am	1.52×10^{2}	4×10^{-3}	3.65×10^{-1}	1.46×10^{-3}
^{243}Am	7.4×10^{3}	7×10^{-3}	3.65×10^{-1}	2.55×10^{-3}
^{244}Cm	1.8×10^{2}	2.8	3.71×10^{-1}	1.05
^{245}Cm	8.5×10^{3}	6×10^{-3}	1.24×10^{-1}	7.41×10^{-4}
Total			1.20×10^{2}	2.56

Conclusions

The development status of the Sphere Pac fuel production has been presented at PSI. Based on the results obtained with cerium solution, microwave internal gelation is a promising route for the fabrication of MA doped fuels and 2 mm diameter cerium-based spheres could be produced. The interaction of the electric field in the cavity with the drop has been modelled and provides optimisation of the further cavity designs. Some developments remain to be performed before the production with active (and namely MA) solution can be achieved, however, the microwave heating unit is already sufficient.

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