Milestone 42
Delivery of wet oxidation samples to HIP

Date 24.08.2022

Dissemination level: Public

Sam Walling

The University of Sheffield (USFD)

Department of Materials Science & Engineering
Sir Robert Hadfield Building
Mappin Street
Sheffield
S1 3JD

s.walling@sheffield.ac.uk

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. MS42	Milestone title Delivery of wet oxidations samples to HIP		
WP No WP6	Date version 24.08.2022		Due date M24
Lead beneficiary The University of Sheffield (USFD)			
Main author Sam Walling (USFD)	Reviewed by Thierry Mennecart, WP6 lead (SCK CEN)	Accepted by Maria Oksa, Coordinator (VTT)	
Contributing author(s)			Pages 4

Abstract

This report summarises the successful delivery of wet oxidation sludges and derived simulant material for HIP processing at USFD.

Coordinator contact

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

Acknowledgement

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

1 Milestone Description

Milestone # 42, associated with Work package 6, Task 5 has been completed on 24.08.2022.

The justification for the readiness is described below and complies with the Grant Agreement Description of Action noting verification by delivery of samples.

The readiness of the milestone was reviewed and agreed upon by Thierry Mennecart (SCK CEN) as WP6 Leader.

2 Delivery of wet oxidation samples to HIP

USFD has been studying the use of Fenton wet oxidation to degrade and destroy organic ion exchange resins. At Sheffield this was achieved through the use of H_2O_2, 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 required to be delivered for use in WP 6.5.

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. 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 H_2O and CO_2, resulted in only small quantities of separated, dried sludge produced per run (<0.2 g).

X-ray diffraction of the dried sludge (Figure 1) 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.

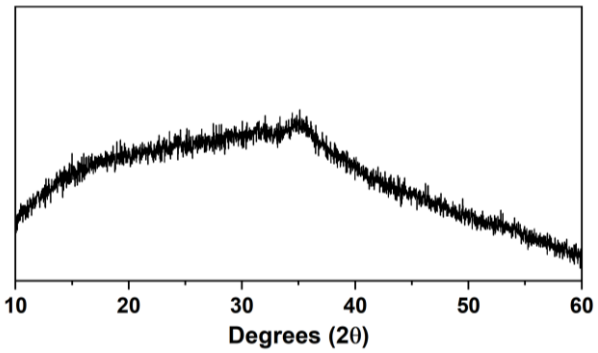

Figure 1. XRD pattern of precipitated, dried wet oxidation sludge

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*

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 2 shows the XRD pattern for the heated wetox material, revealing a crystallised mixture of Fe_2O_3 and CuO. These compounds are readily commercially available in large quantities to enable both small- and large-scale HIP trials.

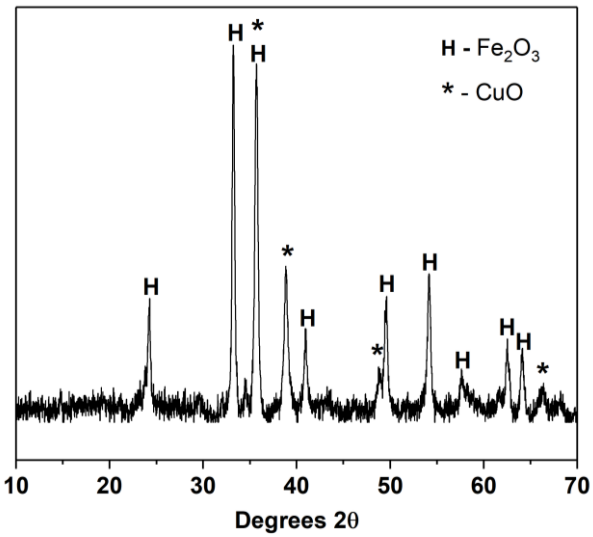

Figure 2. XRD pattern of the sludge heated to 600 °C

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.