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Recovery of zirconium from pickling solution, regeneration and its reuse

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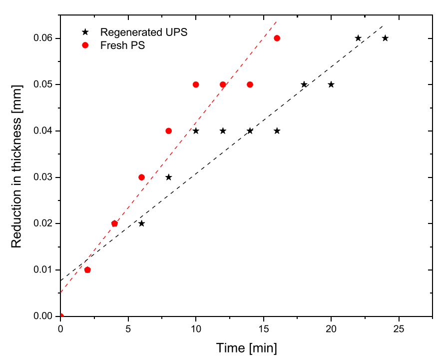
HIGHLIGHTS

- Pickling of zircaloy tubes and appendages is carried out to remove oxide layer.
- The pickling solution become saturated with zirconium due to reuse.
- As $NaNO_3$ concentration increases, conc. of Zr in pickling solution decreases.
- Experimental results shows that, used pickling solution can be regenerated.
- Regenerated solution may be reused by adding makeup quantities of HF-HNO_3.

GRAPHICAL ABSTRACT

The following compares the performance of fresh pickling solution (PS) and regenerated and used pickling solution (UPS).



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ABSTRACT

The pressurized heavy water reactors use natural uranium oxide (UO_2) as fuel and uses cladding material made up of zircaloy, an alloy of zirconium. Pickling of zircaloy tubes and appendages *viz.*, spacer and bearing pads is carried out to remove the oxide layer and surface contaminants, if present. Pickling solution, after use for many cycles *i.e.*, used pickling solution (UPS) is sold out to vendors, basically for its zirconium value. UPS, containing a relatively small concentration of hydrofluoric acid. After repeated use, pickling solution become saturated with zirconium fluoride complex and is treated by adding sodium nitrate to precipitate sodium hexafluro-zirconate. The remaining solution can be recycled after suitable makeup for further pickling use. The revenue lost by selling UPS is very high compared to its zirconium value, which causes monetary loss to the processing unit. Experiments were conducted to regenerate and reuse UPS which will save a good amount of revenue and also protect the environment. Experimental details and results are discussed in this paper.

1. Introduction

Zirconium (Zr) is a precious metal in the nuclear industry. Its unique properties *viz.*, high mechanical strength, low neutron absorption cross section and high corrosion resistance enables it to be used for fuel cladding, pressure and calandria tubes and other reactivity control mechanisms in nuclear reactor components (Buijs and Innomet, 2008; Bhattacllarjee et al., 2015). Indian Pressurized Heavy Water Reactors (PHWRs) use oxide of natural uranium, uranium di-oxide (UO_2) as fuel and zircaloy, an alloy of Zr as cladding material. During the fabrication process of zircaloy, different surface impurities and an oxide layer get deposited on the zircaloy tubes and structural materials, *viz.* spacer pads and

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bearing pads. These surface contaminants, if not removed from the finished zircaloy product, may cause problems in the operation of the nuclear reactor. These surface contaminants and oxide layer are normally removed by pickling process (Walker, 1992; Megy and Propst, 1978). However, much information is not available in literature, since the process has specific application and has commercial importance. This paper discusses the process of pickling of zircaloy tube and accessories, treatment and recycling of spent pickling solution developed at Nuclear Fuel Complex (NFC), Hyderabad, India.

2. Pickling process

Zircaloy undergoes acid pickling operation during various stages of fabrication. Acid Pickling is a chemical operation in which contaminants on metal surface like oxide film; scales etc. are removed by dipping the material in an acid bath. Pickling of Zircaloy usually is carried out in aqueous solution of hydrofluoric acid (HF) and nitric acid (HNO_3). The composition of pickling bath used in Nuclear Fuel Complex (NFC) is 3% HF, 40% HNO_3 and rest 57% De-Mineralized (DM) water.

Zircaloy products such as fuel tubes in intermediate stages, extruded blanks, hot rolled sheets, intermediate sheets, scrap tubes, tube assembly parts, spacer and bearing pads etc. undergo pickling. Thin layers of surface of metal can also be removed by mechanical operations *viz*., grinding, sand blasting, etc. But pickling is most convenient and economical operation when compared to mechanical operations.

Interaction of Zircaloy with HF is associated with formation of a strong Zr-F bonds and fluoro-zirconic complexes. Zirconium dissolves in aqueous HF with the evolution of hydrogen and the formation of hexa-fluoro-zirconic acid (H_2ZrF_6) in solution. The oxide layer too reacts to form hexa-fluoro-zirconic acid. Probable Reactions (1–5) take place during pickling.

$$Zr + 6HF + 4HNO_3 \rightarrow H_2ZrF_6 + 4NO_2 + 4H_2O \quad (1)$$

$$3Zr + 18HF + 4HNO_3 \rightarrow 3H_2ZrF_6 + 4NO + 8H_2O \quad (2)$$

$$3Zr + 4HNO_3 + 12HF \rightarrow 3ZrF_4 + 4NO + 8H_2O \quad (3)$$

$$ZrF_4 + 2HF \rightarrow H_2ZrF_6 \quad (4)$$

$$ZrO_2 + 2HF \rightarrow H_2ZrF_6 + 8H_2O \quad (5)$$

2.1. Role of nitric acid in pickling solution

Nitric acid is a commonly used dissolving agent in metallurgical and nuclear industries (Mandal and Ghosh, 2005; Jaiswal et al., 2015) and nitric acid plays important role in pickling solution. Primarily, it controls the rate of reaction and it minimize the ionization of HF. Moreover, it increases the solubility of Zr-F complex and added bright surface finish of the tube after pickling. The choice of acids was made according to their potential in pickling by forming soluble salts with the main components with the compounds to be removed in agreement with published solubility data (Handbook of Chemistry and Physics, 1964–1965).

2.2. Depletion of pickling bath

With usage, the pickling bath gets mild because of the depletion in free HF. In order to reuse the bath, HF has to be added to the solution. But, with repeated use, dissolved Zr content increases in the bath and after saturation limit is reached it precipitates as ZrF_4 salts. If the precipitation takes place on the surface of the Zircaloy, non-uniform pickling would result in thickness variation of tube. Initially formed passive film is removed by high concentration of F^- ions, but as the bath gets mild the layer formed can't be removed by the depleted fluoride concentration, as the fluoride content decreases, as shown in Reactions (1–5).

3. Experiments

Used pickling solution (UPS) from NFC was experimented on and the following observations and remarks were recorded. All the samples experimented on were of 500 ml volumes. The mixing time was maintained constant as 15 min. The concentration results are given after proper multiplication. The iron content in all the samples were in μg/l level and no significant effect was observed. Experiments were carried out at room temperature.

The UPS contains mainly H_2ZrF_6. The following reaction, preferably, occurs in the experiments, after the addition of $NaNO_3$. The product formed, Na_2ZrF_6 (sodium hexaflurozirconate), is a solid white precipitate, insoluble in HF, HF-HNO_3 and aqua regia, as shown in Reaction (6).

$$H_2ZrF_6 + 2NaNO_3 \rightarrow Na_2ZrF_6 + 2HNO_3 \quad (6)$$

Fennemann and Wolfgang (1982) used NaF for UPS treatment. But, the problem with NaF is that it has low solubility in water. Also insufficient addition of NaF leads to $NaZrF_5{\cdot}H_2O$ – a gel like material, difficult to filter. Excess addition may lead to premature precipitation of Na_2ZrF_6 due to common ion effect and may interfere with pickling process after recycle step. From the literature it is also learnt that the solubility of Na_2ZrF_6 decreases as HF content decreases while solubility of Na_2ZrF_6 decreases as HNO_3 concentration increases (Walker, 1992). Based on the literature survey, $NaNO_3$ was used as the reagent to treat the UPS. The $NaNO_3$ used was of 98% purity. Four sets of experiments were carried out.

4. Results and discussions

Figs. 1–4 show the variation of quantities of various components with the change in the quantities of $NaNO_3$ for samples 1–4. Fig. 5 shows the effect of quantity of $NaNO_3$ on nitrate ion content and Fig. 6 shows the effect of quantity of $NaNO_3$ on the amount of precipitate formed.

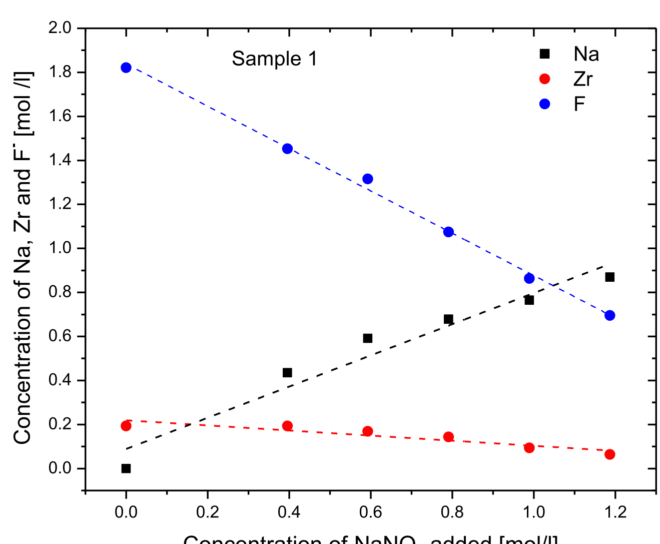

Fig. 1. Effect of quantity of $NaNO_3$ on different components *viz*., Na, Zr and F^- for sample 1(dashed lines are drawn to guide the eye only).