STUDY ON THE DISSOLUTION OF URANIUM DIBUTYL PHOSPHATE DEPOSITS

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Abstract

An insoluble sticky complex of uranium dibutyl phosphate (U-DBP) formed on the inner surfaces of a reprocessing facility can host radioactive nuclides resulting in radiation exposure hazard. Removal of this layer will greatly result in the reduction of radiation field. Hence, dissolution studies with synthetically prepared U-DBP were carried out.

A two-step dissolution process consisting of an initial oxidation with acid permanganate followed by reduction with NAC (NTA, Ascorbic acid and Citric acid) was used. Oxidation kinetics of DBP by permanganate, dissolution of synthetic U-DBP complex as a powder and also as a film over SS surface was studied. XRF and SEM technquies were used to monitor the process of dissolution. Material compatibility of welded SS-304 specimens was also studied. It was found that the two-step process was more efficient when compared to either permanganate or NAC treatment alone

1. Introduction

During the operation of reprocessing plants or on long storage of reprocessing wastes, the tributyl phosphate (TBP) which is used in the solvent extraction step of PUREX[1,2] process gets hydrolysed to form dibutyl (DBP) and monobutyl (MBP) phosphates. The solubility of metal complexes of these hydrolysed products especially uranium complex of DBP (U-DBP) is quite low and hence forms a sticky coating on the surfaces[3], which may host the radioactive nuclides and fission products and thereby result in radiation exposure hazard.

Dissolution of so formed organic layer along with radio active nuclides will result in the reduction of radiation field around the reprocessing plants. Hence, studies with synthetically prepared uranium dibutyl phosphate were carried out to arrive at a suitable chemical formulation/process to dissolve the layer efficiently.

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2. Methods and materials

All chemicals used were of AR/GR grade and the solutions were prepared either in de-mineralized or double distilled water.

2.1 Estimation of uranium

2.1.1 XRF

PW 4025 Mini Pal energy dispersive X-ray spectrometer was used for the estimation of uranium. 200µl aliquot of the sample was dried under IR lamp over PPF film and the spectrum was recorded to carryout both qualitative and quantitative estimations. There was no interference from other ions.

2.1.2 UV-Visible spectrophotometry

In some experiments, uranium was also estimated spectrophotometrically at 304nm as its yellow colored thiocyanate complex by complexing it with ammonium thiocyanate in alcoholic medium. A standard calibration graph (Concentration Vs Absorbance) with known concentrations of uranium was obtained which was linear in the range 0 – 15ppm with a slope of 21.6 and intercept of 0.1.Thus,

$$\text{Concentration of U in ppm} = (\text{Absorbance} \times 21.6) + 0.1 \tag{1}$$

2.2 Estimation of potassium permanganate

Permanganate is estimated spectrophotometrically at 536nm. It was confirmed that there was no interference from uranium. A standard calibration graph (Concentration Vs Absorbance) for known concentrations of permanganate was obtained which was linear in the range 0 – 50ppm with a slope of 76.3 and intercept of 0.2. Thus,

$$\text{Concentration of } MnO_4^- \text{ in ppm} = (\text{Absorbance x } 76.3) + 0.2 \tag{2}$$

3. Experimental

3.1 Preparation of U-DBP complex and its coating over SS coupons

The U-DBP complex was prepared by solution precipitation by adding a suspension of DBP in HNO_3 to a solution containing uranium in HNO_3. The precipitate was digested for about an hour at 60-70°C, filtered, washed and dried at 100°C till constant weight was obtained. On analyzing, the percentage composition of uranium in the complex was found to be around 10.

The coating of the complex on the SS coupons were obtained by immersing 2 sets of coupons; one set polished to diamond grit and the other polished to 220 grit during the solution precipitation of U-DBP complex. The coupons were dried in oven at 100°C for 24h. The thickness of the coating was roughly estimated to be around 4-6µm.

3.2 Dissolution experiments

All dissolution experiments were carried out in a table-top set-up consisting of 250ml round bottomed flask with a provision to purge inert gas. The contents of the flask were stirred and heated using a heater-cum-stir mantle. Observations showed that the rate of dissolution was quite slow and hence most of the experiments were carried out for long duration (24 hours) to achieve appreciable dissolution, while dissolution of U-DBP coating from the SS surfaces was done for only 6 hours.

3.3 Material compatibility experiments

Compatibility of the structural materials in the formulation at welded joints was studied by exposing welded and control specimens of SS-304 to the formulation containing potassium permanganate and nitric acid (NP reagent) for 24 hours. The solution was then neutralized by citric acid to decompose permanganate. The metal coupons were washed, dried, weighed and then exposed to NAC formulation (a mixture of NTA, ascorbic acid and citric acid) for 24 hours. At the end of the experiment, the coupons were removed, washed, dried, weighed and subjected to detailed metallographic examination.

4. Results and discussions

Reprocessing plants are prone to high radiation exposure hazard owing to their inherent capabilities of handling highly radio-active materials such as used fuel pins[4]. It handles tributyl phosphate (TBP) which is one of the solvents used during the solvent extraction process in separating uranium and plutonium from other fission products. TBP tends to hydrolyse to dibutyl (DBP) and monobutyl (MBP) phosphates.

$$\underset{\text{TBP}}{[CH_3(CH_2)_3O]_3 - P = O} \xrightarrow{H_2O} \underset{\text{DBP}}{[CH_3(CH_2)_3O]_2 - P(OH) = O} + CH_3(CH_2)_3OH \tag{3}$$

$$\underset{\text{TBP}}{[CH_3(CH_2)_3O]_3 - P = O} \xrightarrow{2H_2O} \underset{\text{MBP}}{[CH_3(CH_2)_3O] - P(OH)_2 = O} + 2CH_3(CH_2)_3OH \tag{4}$$

It is reported that on long standing of reprocessing wastes containing uranium and other fission products along with TBP and its hydrolysed products such as DBP and MBP, an insoluble sticky complex of U-DBP is formed. The precipitation of U-DBP and the nature of the complex are dependent on the concentration of DBP, pH and the concentration of nitrate ions in the solution[3].

At low acid concentration :

$$UO_2^{2+} + 2DBP^- \rightarrow \underset{\text{solid}}{UO_2(DBP)_2} \qquad (5)$$

At high acid concentration and high NO_3^- ions :

$$\mathrm{UO}_2^{2+} + 2DBP^- + HNO_3 \rightarrow \underset{\text{solid}}{UO_2(NO_3)_2(DBP)_2} \qquad (6)$$

At high concentration of DBP :

$$UO_2^{2+} + 4DBP^- \rightarrow [UO_2(DBP)_4]^{2-} \qquad (7)$$

The sticky complex of U-DBP formed during the operation of reprocessing plants along with the corrosion products get deposited on the structural materials and act as host for radio-active nuclides and other fission products resulting in radiation exposure hazard. Hence, removal of these radio-active nuclides by the dissolution of U-DBP layer along with corrosion products will reduce the risk of radiation exposure. Thus, a study on the dissolution of U-DBP complex, which was synthesized via solution-precipitation was carried out.

4.1 Dissolution formulation

The structural material of the reprocessing plant is mainly stainless steel, which invariably has a protective oxide coating of Cr_2O_3 along with iron and nickel substituted chromites[5]. Literature and experience confirms that the oxide layer on SS is removed effectively by the combined action of oxidation and reduction processes[6,7]. Permanganate based formulations are the preferable oxidizing agents while a mixture of organic acids are the preferable reducing agents[8,9,10]. U-DBP complex, being organic in nature, will also be solublized by such an oxidizing process followed by acid treatment. Hence, the dissolution studies were carried out with formulation containing 5mM nitric acid and 2.5mM potassium permanganate (NP reagent) as oxidizing agent[11] and a mixture of 1.4mM NTA, 1.7mM ascorbic acid and 1.4mM citric acid (NAC formulation) as reducing agent[12].

4.2 Oxidation of DBP by NP formulation

Studies were carried out to understand the kinetics of oxidation of pure DBP by NP reagent at 80°C. Varying amounts of DBP was added to NP reagent and the oxidation was monitored by estimating the concentration of permanganate in solution (Figure 1). It was observed that, as long as there was enough permanganate in solution, the oxidation isotherm was linear with time. Also, it was seen that the rate of oxidation was dependent on the initial concentration of DBP (Table 1).

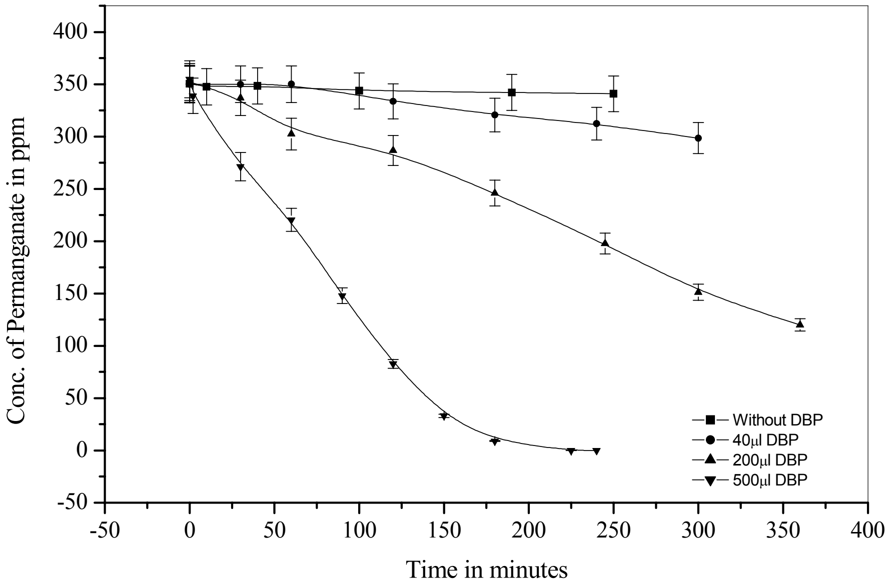


Figure 1 Consumption of Potassium Permangante during the oxidation of Dibutyl Phosphate

Table 1 Rate of decomposition of potassium permanganate versus initial concentration of DBP at 80°C

(Values extracted from figure-1)

Volume of DBP added to the system in μl	**Rate of decomposition of $KMnO_4$ in ppm/min**
40	-0.18
200	-0.65
500	-2.13

4.3 Powder dissolution of U-DBP complex

300mg of the U-DBP complex as powder was exposed to 250ml of NP reagent for about 6 hours. The process of dissolution was followed by monitoring concentration of both permanganate and U in solution by spectrophotometry and XRF respectively. The curve obtained for the U build-up with time (Figure 2) was found to be logarithmic. On calculation, it was seen that at the end of 6 hours around 20% dissolution of U-DBP complex was achieved.

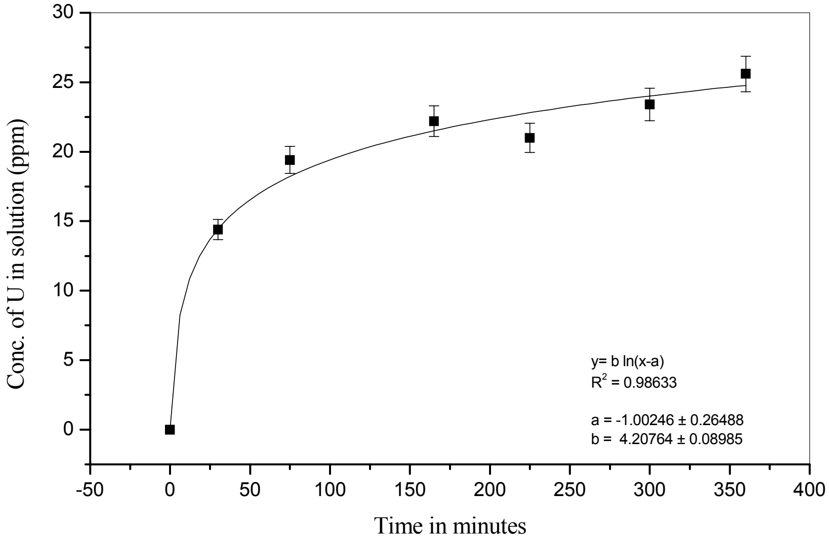


Figure 2 Build-up of U in solution during the dissolution of U-DBP in NP reagent at 80°C

The above dissolution experiment was also carried out at a lower temperature of 65°C. Besides, experiments were also carried out at 80°C with NAC formulation (reducing treatment) alone and in a two-stage process involving exposure to oxidizing NP formulation followed by reducing NAC formulation. Figure 3 compares the results obtained therein.

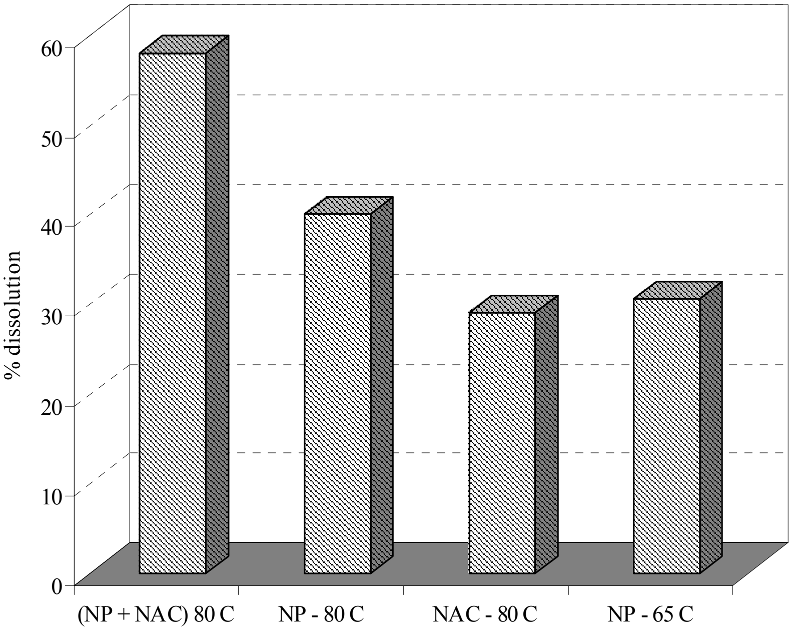


Figure 3 Dissolution of U-DBP powder under different conditions

From the above graph it is seen that the dissolution of U-DBP complex is more effective if the complex is subjected to oxidizing treatment followed by acid treatment. Besides, higher the temperature higher is the dissolution.

4.4 Dissolution U-DBP coated as a film over SS coupon

The dissolution behaviour of powder is normally different from the dissolution of a film. Hence, dissolution studies were also carried out with U-DBP film coated over SS coupons. The U-DBP coated coupons were exposed to NP reagent for 6 hours. At the end of 6 hours, the coupons were removed and the solution was filtered. The coupons, residue and the filtrate were analysed for U by XRF.

Figure 4 shows the metallographic examination by SEM before and after exposure to the NP reagent. Figure 5 gives the XRF spectrum of the specimen before and after exposure. It is seen that the spectrum showed a prominent peak for U at 13.6 keV before exposure while there was no such peak after exposure.

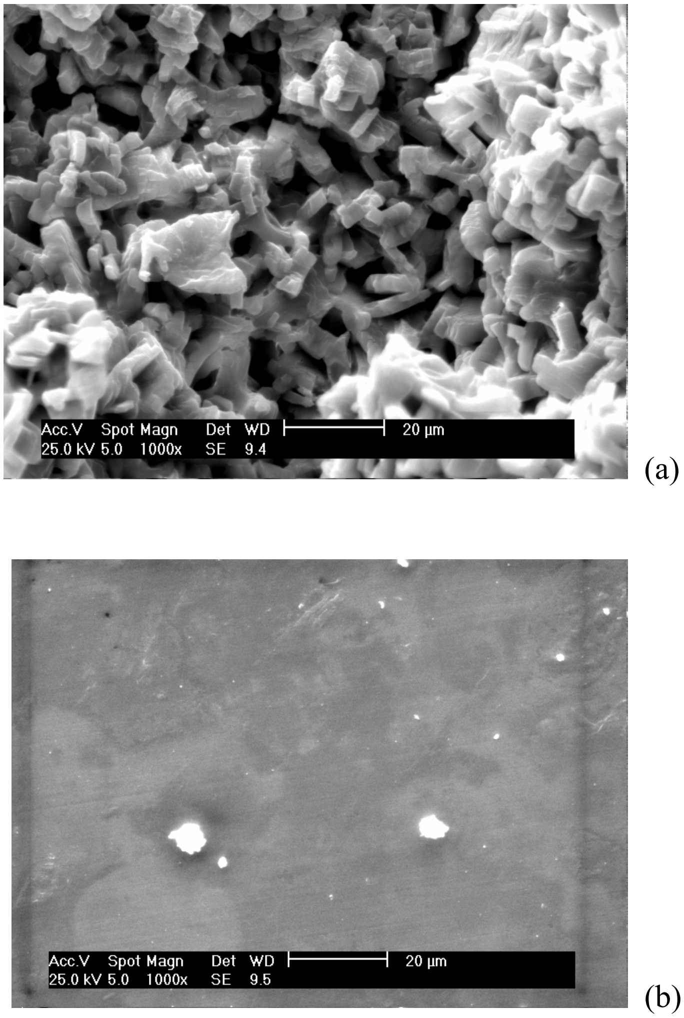


Figure 4 SEM showing the U-DBP coated SS coupons before (a) and after (b) exposure to NP reagent at 80°C

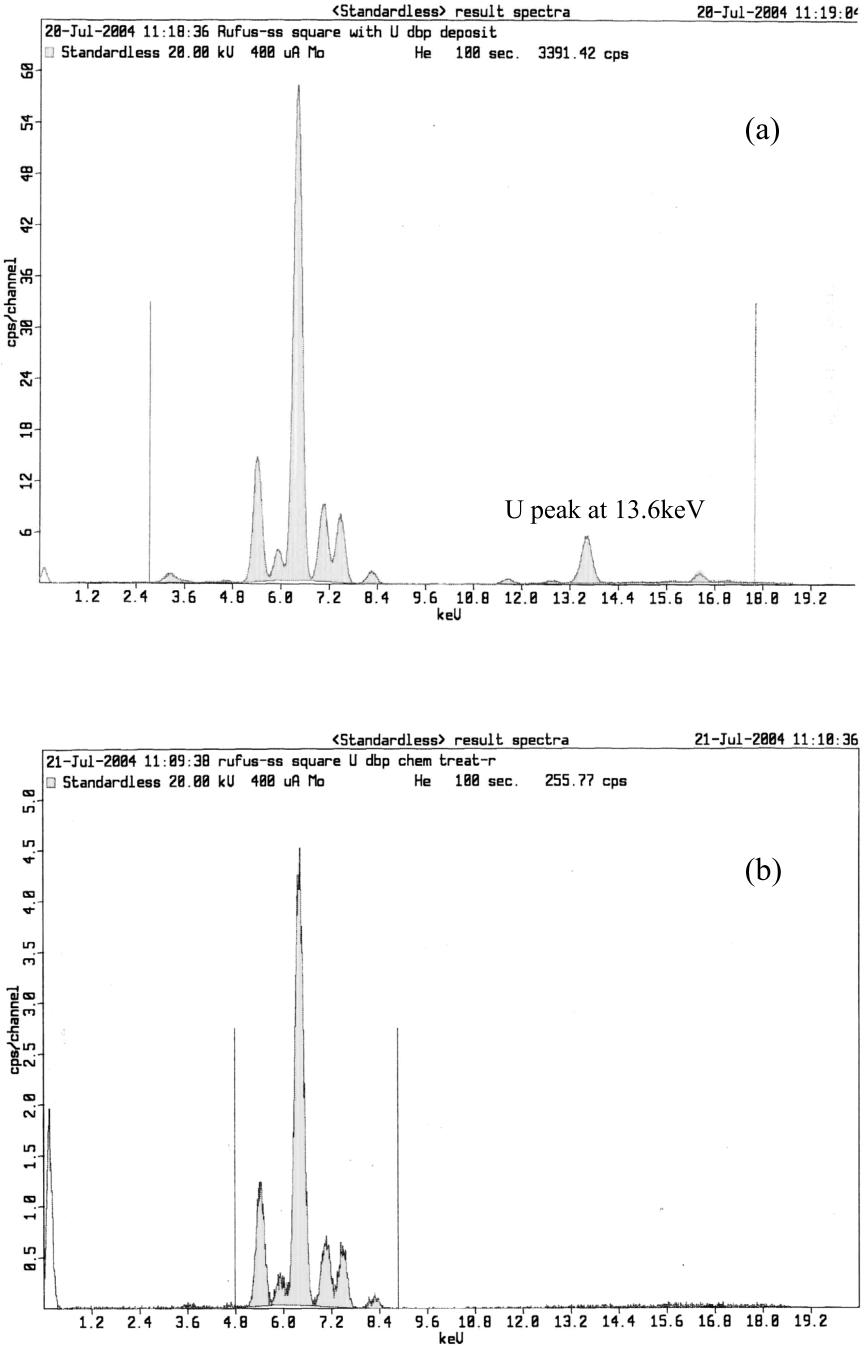
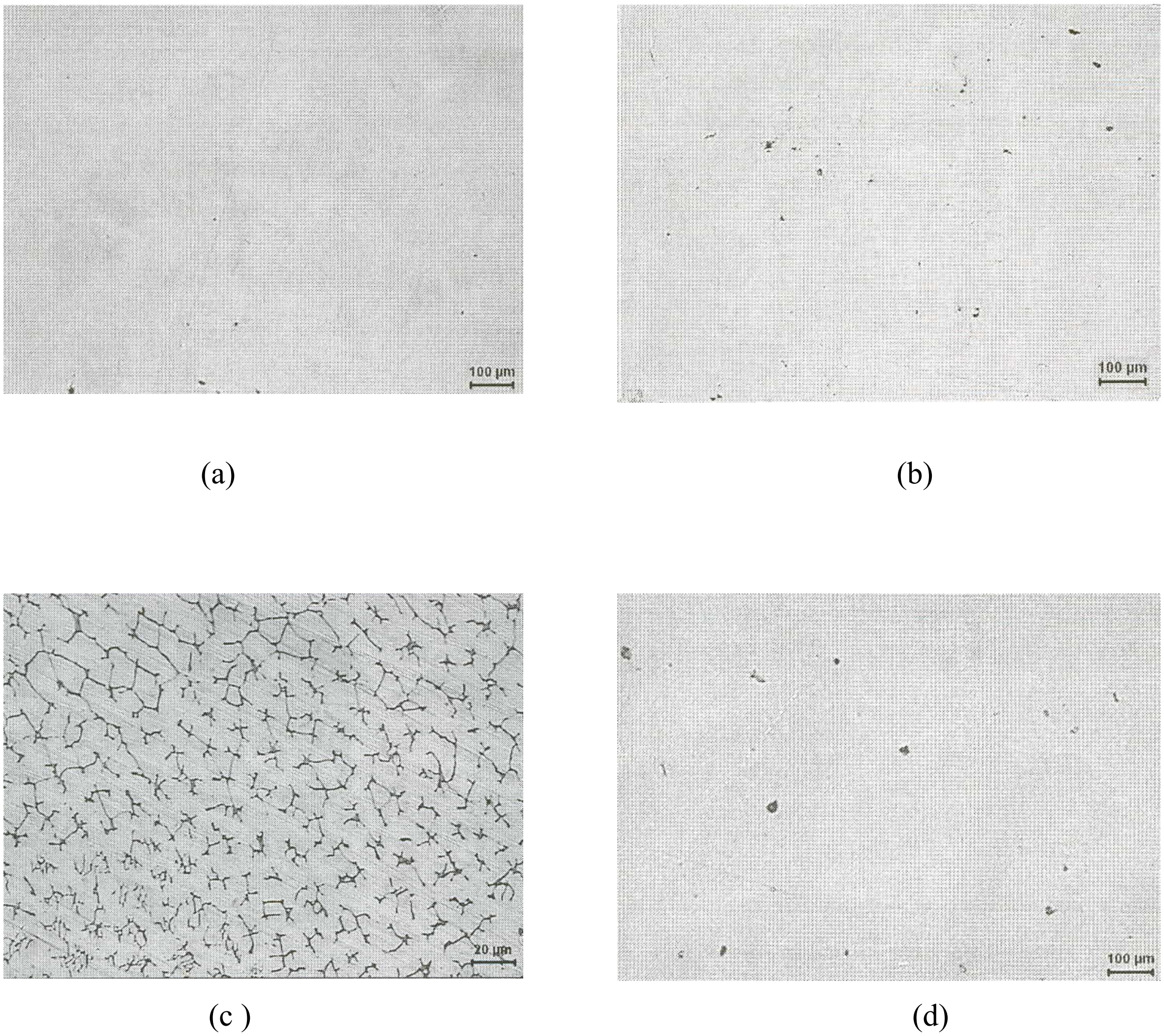


Figure 5 XRF spectrum showing the U peak for U-DBP coated SS coupons before (a) and after (b) exposure to NP reagent at 80°C

Analysis of the filtrate showed 90% dissolution of U-DBP coating while <1% was remaining on the surface. The remaining unaccounted uranium would have been co-precipitated along with MnO_2. This was confirmed by the XRF analysis of the residue which showed the characteristic peak for uranium.

4.5 Material compatibility

A three stage exposure of the welded specimens of SS 304 and control coupons were carried out to assess the material compatibility of the structural material with the NP reagent. The first stage was exposure of the coupons for 24 hours to NP reagent and followed by the addition of citric acid to decompose any unused permanganate and the precipitated MnO_2. The coupons were then exposed for 24 hours to NAC formulation. Fig.6 (a-d) shows the detailed metallographic examination of the exposed and unexposed coupons. It was concluded from the micrographs that both the control and the weld metal showed typical etching type of light attack accompanied by dissolution of the surface inclusions and formation of etch pits. Thus, the formulations are effective in dissolving U-DBP layer with minimum corrosion of the structural materials.



(a) (b)

(c) (d)

Figure 6 Metallographic examination of control and weld metal exposed to NP formulation
(a) Control before exposure (b) Control after exposure
(c) Weld metal unexposed metallographically etched (d) Weld metal after exposure

5. Conclusions

i. The kinetics of oxidation of DBP by potassium permanganate was found to be linear as long as there was enough permanganate in solution. Besides, the rate of oxidation was found to be dependent on the initial concentration of DBP.

ii. Dissolution isotherm of U-DBP complex as powder in NP reagent followed a logarithmic fit.

iii. A two stage process consisting of preliminary oxidizing step followed by acid dissolution is more effective in dissolving U-DBP rather than only oxidizing or only reducing step.

iv. Both NP reagent and NAC formulation are compatible with base metal and hence U-DBP film can be safely dissolved with permissible corrosion effects.

v. Before the application of the process to a reprocessing plant, its effectiveness should be tested in a pilot plant on representative specimens. Further, waste management of the resulting active solution should also be considered before any such field application.

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