



Solvent degradation—Rössing Uranium Mine

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Synopsis

Rössing Uranium Mine operates a recovery circuit with continuous ion exchange followed by solvent extraction. Serious organic degradation problems were encountered during 1985/6, 2000 and 2005 in the solvent extraction plant. The preferential loss of the tertiary amine extractant was observed during the above-mentioned period. Previous investigations revealed that the tertiary amine was breaking down to nitrosamine, which cannot take part in the exchange reaction with U_3O_8 . A reduction in the redox potential of the solvent extraction plant feed to below 500 mV halted this preferential loss.

A lot of effort has been made to try and understand the actual mechanism for nitrosamine formation. Current understanding for the degradation is that formation is due to high nitrates on the strip side of the circuit emanating from nitrates from the precipitation process using ammonia. It is the current belief that pH lower than 3.7 on the strip side results in loading of nitrates onto the solvent. If oxidizing conditions prevail on the extraction side of the solvent extraction circuit, the tertiary amine will then degrade into nitrosamine. This phenomenon is yet to be established and verified.

It has, however, been established that the above process is brought about the following conditions

- ▶ High redox potential greater than 550 mV predominately caused by a high Fe^{3+}/Fe^{2+} ratio (4:1)
- ▶ Perception that if $Fe^{2+} < 0.5$ g/l it will contribute to high redox
- ▶ High concentrations of NO_3^- in the conc eluate (feed to SX)/ammonium sulphate ($NO_3^- > 4$ g/l based on historic values)
- ▶ Presence of Mo as a catalyst
- ▶ Tests also have proved that the presence of nitrous acid in a concentration of 1 g/l at 550 mV leads to formation of nitrosamines from alamine.

Historical background

Rössing Uranium Mine has a low grade uranium orebody. The uranium processing plant comprises four stages of crushing, leaching, liquid-solid separation, ion exchange, solvent extraction and precipitation.

The solvent extraction plant (SX) is the second concentration/purification plant at Rössing Uranium Mine in which it concentrates U_3O_8 in a conc eluate solution to the OK liquor, typically from 5 g/l to 15 g/l. It is a countercurrent process with a five-stage

extraction section, a two-stage scrub section and a four-stage stripping section. In the extraction section, the solvent medium is loaded with U_3O_8 ; in the scrub section the loaded solvent is washed with fresh water to remove unwanted co-extracted impurities as well as entrained aqueous; while in the strip section the solvent is stripped of U_3O_8 .

The standard solvent for Rössing Uranium Mine solvent extraction plant is Alamine 336 at 7 per cent (v/o) plus Isodecanol, 3 per cent (v/o) in an SSX210 (aliphatic) diluent. Over the years degradation of tertiary amine (extractant) has been experienced. It dates back to 1972 during the pilot plant studies.

In 1972 during operation using a bufflex type process, solid ion exchange followed by solvent extraction treatment of the eluate, the amount of uranium remaining in the organic phase leaving the strip section of the solvent extraction plant steadily increased. A preliminary investigation of the problem by the National Institute of Metallurgy in South Africa led them to suggest that sodium chlorate oxidation of a portion of the active ingredient of the solvent mixture yielded a ketonic compound, which was responsible for this phenomenon.

The possibility of bacteriological contamination was investigated. There was no evidence of the activity of microorganisms in any of the samples submitted, and most of them appeared to be sterile or very nearly so. The conclusion reached was microorganisms did not interfere with the process.

In March 1985 a preferential loss of tertiary amine was noticed. This continued throughout the remainder of 1985 into 1986. Considerable efforts were made to identify the loss mechanism; however, they were unsuccessful. In June 1986 it was recommended by Dr Lewis during his consul-

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tative visit that the SX feed solution redox potential be reduced to a maximum of 550 mV from the then present levels of just below 700 mV. It was believed that this would stop oxidative breakdown of the alamine. Mild steel wire was added to the overflow weirs of extract 5 to achieve this. The preferential loss of alamine was not stopped until day 35 of the trial (25 July) when the redox potential in both raffinate and conc. Eluate were reduced to below 510 mV. This was achieved by levelling the redox potential profile through the extraction circuit by adding wire to the overflow weirs of extract 1 and 3 in addition to extract 5.

In 1993 week 38 a sudden drop in extraction efficiency was experienced in the solvent extraction. Loaded solvent tenors dropped by approximately 20% and raffinate tenors increased. Despite regular wire addition into the overflow weirs of the raffinate settlers the redox potential stayed above 500 mV with excursions above 520 mV. Samples taken at overflow weirs of the mixer/settlers in the extraction section on SX indicated that there was an increase in redox potential from extraction settler 1 (E1) to extraction settler 5 (E5). During investigation into the problem the following were noticed:

- ▶ Concurrent with the increase in redox potential there was a decrease in tertiary amine concentration of the solvent
- ▶ Although ammonium sulphate stripped NO_3^- from the loaded solvent there was little or no difference in the nitrate concentrations in the loaded and stripped solvent, i.e. little NO_3^- removal.

Towards the end of 1999, solvent extraction performance (as measured by extraction efficiency) began to deteriorate sharply, while simultaneously preferential tertiary amine losses rose. The deterioration in performance was similar to events in 1985 and 1993. In 2000 the whole organic was replaced with fresh organic due to a high level of degradation products. The solvent was dark in colour and increased phase disengagement time.

In 2001 a portion of contaminated/degraded solvent was bled into the circuit after initial tests conducted in Rössing Uranium Limited laboratory indicated that it was no longer as contaminated as when it was removed from the plant (for reasons that were not understood). The tests were not representative of plant conditions. An immediate increase in redox potential was observed after bleeding the contaminated organic into the circuit. Redox potential in conc eluate (feed to SX) and raffinate increased to level above 520 mV. A decrease in the concentration of tertiary amine was observed in weekly analysis; this was coupled with decrease in SX extraction efficiency. Alamine 336 concentration decreased from 7% to 5%. The circuit recovered after topping up amine to 7%, in the process diluting the nitrosamine concentration.

In 2005, two incidents of high redox potentials were experienced. The first one happened in the period between 10 and 19 March with redox running as high as 700 mV. The second one occurred from 13 May with redox potential of 550 mV and above. This period extended up to 2 June. The former incidence was quenched by the excessive addition of 8 200 litres of alamine 336 when alamine strength dropped from 7% to 4%. This alleviated the situation, and the SX operated as normal until 12 May when the incident occurred again. This time around, there was no alamine available on site to resuscitate the solvent. The conc eluate redox potential

remained above 550 mV despite the addition of 1 000 kg of wire per week in all the SX extraction settlers and Conc sumps at CIX. The redox dropped only when the ferrous levels picked up to about 2 g/l. A decision was made to replace the entire organic inventory using fresh Shellsol 2325, Isodecanol and alamine 336 because of high levels of nitrosamine.

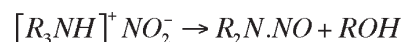
Investigating the cause of degradation

In 1986 two solvent samples from Rössing Uranium solvent extraction plant were examined by Warren Spring Laboratory using infrared spectroscopy and gas chromatography-mass spectrometry (GC-MS) for possible degradation products of extractant, Alamine 336. Both were found to contain nitrosamines and secondary amines, which were not present in fresh solvent.

According to the literature, nitrosamines are formed by the action of nitrous acid on secondary amines:



Tertiary amines also react with nitrous acid to form the nitrite salt, R_3NHNO_2 or $[R_3NH]^+NO_2^-$. When this is warmed the nitrite decomposes to form a nitrosamine and alcohol.



It was concluded that it was unlikely that nitrosamines were formed in the plant solvent by direct action of nitrous acid on the alamine 336 as the plant aqueous phase contained little or no nitrite ions. The feed liquor, however, contained nitrate ions. Thus it was strongly suspected that the loss of amine was associated with nitrate loading on to the solvent because in a pilot plant study carried out at the Government Metallurgical Laboratory (now Mintek) on the Bufflex Project in South Africa in 1964 severe solvent degradation occurred when the plant was operated using nitrate strip. Although in the 1964 study the degradation products of amine extractant were not identified, it was confirmed that nitrate was causing the degradation by storing the amine (in nitrate form) for several days at 70°C after which it was found that the final organic phase showed the same symptoms of degradation as the plant solvent.

To find out whether nitrate ions were contributing to the amine degradation in Rössing plant, a sample of fresh solvent was converted to the nitrate from using dilute nitric acid and then stored for three days at 70°C before analysis by GC-MS. From the GC scan nitrosamine was identified. Neither solvent regeneration with alkali nor steam provided an effective removal of the nitrosamines. Figure 1 shows the level of nitrosamine in plant solvent during the period 1986 to 1987.

Control measures

After the SX disaster in 2005, recommendations were made about controls in the plant to prevent a repeat incident. Table I contains the agreed controls during the exercise.

Additional/more frequent monitoring was introduced of key elements NO_3^- , nitrosamine analysis, $\text{Fe}^{2+}/\text{Fe}^{3+}$, redox, water dilution in ammonium sulphate stream. Standard instructions were formulated to ensure control of ferrous, soluble wire addition and redox control. The type of diluent was changed from aromatic to aliphatic.

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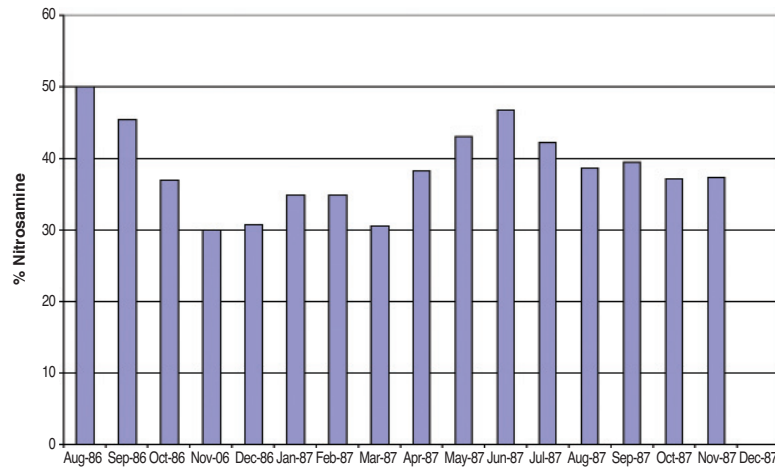


Figure 1—Nitrosamine in plant solvent 1986–1987 (as % of total amine)

Stream	Redox mV	H ₂ SO ₄ g/l	Fe ²⁺ g/l	Fe ³⁺ g/l	NO ₃ ppm	Ammonium Sulphate g/l	H ₂ O (m ³ /day)
Pregnant solution	450–480	2.4–4	>1	0–4	X—Y (no figures specified)	80–85	250–350
Fresh eluate	450–480	95–105					
Conc eluate	450–480	70–90	2–3	0–5			
Ext 1-5	450–480				0–250		
Stripped solvent					<2500		
Ammonium sulphate							

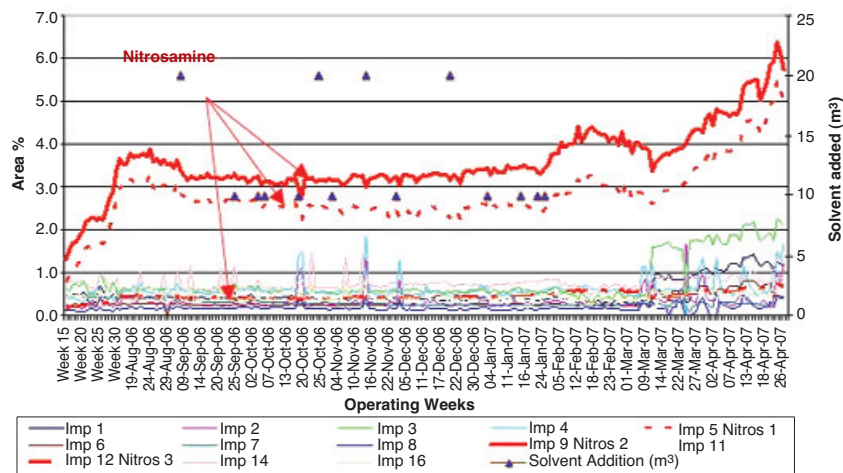


Figure 2—Component composition of impurities in stripped solvent (excluding carrier and modifier)

Current reality

There has been increasing concentration of nitrosamine in the organic/solvent as from 12 March 07, see Figure 2, and redox above 500 mV in SX conc eluate and raffinate streams as from 24 March. Redox was brought under control by addition of soluble wires. During the period when nitrosamine started forming a drop in strip pH below the control target of 4–4.3 allowed the migration of nitrates onto the solvent. Nitrates are the likely candidate for nitrosamine formation at present.

Way forward

The dosage of antioxidant (merisol butyl hydroxy toluene) is being considered to prevent oxidation degradation of tertiary amine. Perhaps one solution to the problem is to remove the

nitrate in a separate small circuit with an amine followed by stripping quickly to minimize amine degradation in that circuit.

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