Solvent degradation—Rössing Uranium Mine
by B.M. Munyungano*

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 $\text{U}_3\text{O}_8$. 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 oxidising 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 by the following conditions

- High redox potential greater than 550 mV predominantly caused by a high $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio (4:1)
- Perception that if $\text{Fe}^{2+} < 0.5\text{ g/l}$ it will contribute to high redox
- High concentrations of $\text{NO}_3^-$ in the conc eluate (feed to SX)/ammonium sulphate ($\text{NO}_3^- > 4\text{ g/l}$ 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 amine.

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 $\text{U}_3\text{O}_8$ 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 $\text{U}_3\text{O}_8$; 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 $\text{U}_3\text{O}_8$.

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-

* Rössing Uranium Limited. © The Southern African Institute of Mining and Metallurgy, 2007. SA ISSN 0038–223X/3.00 + 0.00. This paper was first published at the SAIMM Conference, Uranium in Namibia, 14–16 May 2007.
Solvent degradation—Rössing Uranium Mine

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 amine. Mild steel was added to the overflow weirs of extract 5 to achieve this. The preferential loss of amine 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 NO₃ from the loaded solvent there was little or no difference in the nitrate concentrations in the loaded and stripped solvent, i.e. little NO₃ 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 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 nitric acid on secondary amines:

\[
R_3NH + HNO_2 \rightarrow R_3N \cdot NO + H_2O
\]

Tertiary amines also react with nitric acid to form the nitrite salt, R₃N(NO₂), or \([R_3NH]^+NO_2\). When this is warmed the nitrite decomposes to form a nitrosamine and alcohol.

\[
[R_3NH]^+NO_2 \rightarrow R_3N \cdot NO + ROH
\]

In conclusion it was unlikely that nitrosamines were formed in the plant solvent by direct action of nitric acid on the amine 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 Rossing 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 NO₃, nitrosamine analysis, Fe²⁺/Fe³⁺, 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.
Solvent degradation—Rössing Uranium Mine

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.

References

5. MCKENZIE, J.M.W. Letter from technical manager of Trochem, on alamine degradation product identification, to technical controller. 6 August 1986.