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**RUTHENIUM VOLATILITY FROM THE VITRIFICATION OF
MELTER FEEDS PREPARED USING THE NITRIC ACID
FLOWSHEET (U)**

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**Ruthenium Volatility from the Vitrification of
Melter Feeds Prepared Using the Nitric Acid Flowsheet (U)**

Introduction

The present DWPF flowsheet calls for the chemical treatment of waste sludge with 90 wt% formic acid prior to the addition of the Precipitate Hydrolysis Aqueous (PHA) product. An alternative processing methodology, denoted the "Nitric Acid Flowsheet", has been proposed. In the application of this flowsheet, nitric acid would be used to neutralize sludge base components (hydroxides and carbonates) prior to the addition of late wash PHA. The late wash PHA will contain sufficient quantities of formic acid to adequately complete necessary reduction-oxidation (REDOX) reactions.

The use of this flowsheet may result in a change in the nominal concentrations of two of the major REDOX reaction participants: formate (HCOO^-) and nitrate (NO_3^-).

E. W. Holtzscheiter
Authorized Derivative Classifier

An imbalance in REDOX agents in the melter can result in overly reducing melts which favor the formation and accumulation of metals and metallic sulfides (including selenides and tellurides). Conversely, if the REDOX potential of the melt is imbalanced to the point of being overly oxidizing, there is an increased potential for melter foaming. Further, there may be an increased amount of volatilized ^{106}Ru since nitrates act as oxidizing agents in glass melting and therefore stabilize the highly oxidized, gaseous RuO_4 .

Background

Control of radioactive ruthenium was an early process concern because of expected difficulty in scrubbing out the volatile ruthenium tetroxide (RuO_4)¹. In 1983, Soper² verified thermodynamic calculations which indicated that this species is unstable in the offgas system, decomposing to the scrubbable particulate RuO_2 . Based the kinetics of the decomposition of RuO_4 , Soper estimated that particulate RuO_2 is formed in 0.04 seconds or less in the cool offgas line exiting the melter. This decomposition is catalyzed by different kinds of steels and by RuO_2 itself and does not depend on the amount of ruthenium in the offgas system.

Experimental verification of this result was provided by Klein, et.al.³ This work showed that, even for European waste slurries which are air sparged and very high in nitrates, ruthenium is transported from the melter as particulate RuO_2 . (Note that the study also revealed that the volatilization of Ru was approximately 5 times higher in waste calcination than in direct slurry fed vitrification.) In melting studies at the Savannah River Laboratory, using actual waste, no ruthenium was found past the scrubber section^{4,5,6} even in non-reducing atmospheres.

Ruthenium Volatility in the IDMS Melter

The extent of Ru volatility from the IDMS melter is judged in two ways: (1) analysis of offgas header deposits, and (2) analysis of offgas condensate. Since any gaseous RuO_4 will decompose almost immediately upon entering the offgas exit line, the RuO_2 particulate is likely to deposit on the piping with other volatile and semi-volatile compounds (alkali halides, borates, sulfates) and entrained matter (dried feed, spinels, and frit). And, any RuO_2 particulate entering the quencher would be scrubbed to the condensate.

The offgas header deposits have been analyzed from IDMS runs of various conditions. Samples were taken after using the formic acid flowsheet (for both SRS and Hanford wastes) and after using the nitric acid flowsheet. These samples were analyzed by Scanning Electron Microscopy / Energy Dispersive

X-Ray (SEM/EDX) and by Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES). The results are summarized in the following table:

<u>Run Type</u>	<u>N/F*</u>	<u>Ru (wt%)</u>	<u>Sample Description</u>
Formic Flowsheet (horiz section)	<1.0	< 0.9 %	Not much Ru found, found as oxide but mostly associated with entrained spinels.
HWVP1 (NCAW) ⁷ (horiz section)	1.5	5.2 %	Ru present as oxide, mixed with Rh, Te, and Cd, and associated with spinels.
HWVP2 (NCAW) ⁷ (horiz section)	1.3	2.9 %	Same as HWVP1
Nitric Flowsheet (horiz section)	8 - 16	3.9 %	NA (no SEM/EDX yet)
Nitric Flowsheet (quencher)	8 - 16	1.5 %	NA (no SEM/EDX yet)
* N/F = Nitrate-to-Formate molar ratio NA = Not Available			

Analysis of IDMS offgas condensates have provided limited information on ruthenium volatility since the condensate is normally analyzed by filtering the very small fraction of solids from the liquid before injecting directly into the ICP-AES instrument. RuO₂ is quite insoluble and would mostly be removed from the condensate sample. Analysis of these insoluble solids revealed that they are mostly spinels, Fe₂O₃, AgCl, AgI, and ruthenium. The ruthenium is associated mostly with the spinels but also present as RuO₂ crystals.

To date, no particulate sampling (specifically for Ru compounds) has been conducted in the melter system.

DWPF Design Basis

The material balance tables for the DWPF⁸ predict that approximately 1% of the Ru entering the melter will exit as semi-volatile RuO₂ (particulate aerosol). This assumes that the Ru will first be volatilized to RuO₄ and almost immediately decomposed to RuO₂ in the offgas exit line. The following DF's (Decontamination Factors) have been assumed for the removal of the RuO₂ aerosol:

<u>Offgas Equipment</u>	<u>DF*</u>
Melter	100
Quencher	1
Scrubbers (2)	14
OG Condenser	1
HEME	1
HEPA (stage 1)	200
HEPA (stage 2)	10
Sand Filter	200

* DF = (quantity of RuO₂ in)/(quantity of RuO₂ out)

Conclusions

Melter feeds which are high in nitrates can increase the volatility of ¹⁰⁶Ru due to the formation of the highly oxidized, gaseous RuO₄ during vitrification. However, RuO₄ is very unstable especially at the cooler temperatures of the offgas exit line. Thermodynamic and kinetics calculations have shown that any RuO₄ exiting the melter will rapidly decompose to scrubbable particulate RuO₂. Analysis of IDMS offgas deposit samples suggest that with nitrate-to-formate molar ratios > 1.0 there is an increased amount of Ru in the deposited material (which implies that more Ru is volatilized and/or entrained).

The maximum amount of Ru found in the offgas deposits represents ≈ 1% of the Ru fed to the melter (which corresponds to the assumption made for the DWPF material balances). However, this Ru is mostly found associated with spinel crystals and not as condensed RuO₂.

Since no Ru-specific particulate sampling has been conducted in the melter system, it is not possible to know absolutely the amount of Ru which exits the melter as condensed RuO₂. This is further complicated by the fact that a large portion of the Ru entering the melter settles to and accumulates on the melter floor (so the amount in the offgas cannot merely be assumed to be the difference between that in the melter feed and that in the glass product).

However, all evidence suggests that even if there is an increased amount of Ru exiting the melter with the use of the nitric acid flowsheet, there should not be an increase in the predicted DWPF release rates. The DF's for most of the offgas equipment have been conservatively set. For example, the DF for the 2-stage HEPA is assumed to be 2000 while practical experience has shown this to be as high as 1×10^5 . With this conservatism and the fact that the N/F for the Nitric Acid/Late Wash Flowsheet will change only slightly from the reference (Formic Acid) flowsheet, there are no anticipated increases in ¹⁰⁶Ru emissions from the DWPF.

References

1. D.F. Bickford, R.B. Diemer, and D.C. Iverson, "Redox Control of Electric Melters with Complex Feed Compositions II. Preliminary Limits for Radioactive Waste Melters", *Journal of Non-Crystalline Solids*, 84 (1986) 285-291.
2. P. D. Soper, "Elimination of Ruthenium Absorption Bed", USDOE Report DPST-82-0614, Savannah River Laboratory, Aiken, SC 29808 (1982).
3. M. Klein, C. Weyers, and W. Goosens, "Volatilization and Trapping of Ruthenium in High Temperature Processes", *Proceedings of the 17th DOE Nuclear Air Cleaning Conference*.
4. G. B. Woolsey, and E. L. Wilhite, "Characterization of Off-Gases From a Small-Scale, Joule-Heated Ceramic Melter For Nuclear Waste Vitrification," USDOE Report DP-MS-79-92, presented at the 82nd Annual Meeting of the American Ceramic Society, April 27-30, 1980.
5. G. B. Woolsey, "Off-Gas Characterization From The Vitrification of Tank 15 Waste," USDOE Report DPST-81-666, Savannah River Laboratory, Aiken, SC 29808 (1981).
6. M. J. Plodinec, P. D. Soper, N. E. Bibler, and J. L. Kessler, "SRP Radioactive Glass Studies: Small-Scale Process Development and Product Performance," USDOE Report DP-MS-82-26, Savannah River Laboratory, Aiken, SC 29808 (1982).
7. N. D. Hutson, "Integrated DWPF Melter System Campaign Report: Hanford Waste Vitrification Plant (HWVP) Process Demonstration", USDOE Report WSRC-TR-92-0403, Savannah River Technology Center, Aiken, SC 29808 (1992).
8. A. S. Choi and J. R. Fowler, "Material Balance Tables For The DWPF Basic Data Report (DPSP-80-1033) Revision 138 Appendix G, Table 19-1", USDOE Report WSRC-TR-90-0093, Savannah River Technology Center, Aiken, SC 29808 (1990).

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