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DPST-82-348

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IODINE REMOVAL FROM SRP DISSOLVER OFF-GAS

INTRODUCTION

Iodine-129 and iodine-131 are produced in SRP drivers and targets. Iodine-129 decays by beta emission with a 16 million year half-life and contributes a few percent of offsite dose. Iodine-131 decays by beta emission and gamma emission with a half-life of eight days. Iodine-131 would not be present in fuel dissolved in F-Area unless a short cooled fuel (<180 day) were to be accidentally dissolved during routine processing. Although an accidental release of iodine-131 is a low probability event, it would contribute substantially to off-site dose.

Iodine is partially released to the dissolver off-gas (DOG) during reprocessing. SRP removes iodine from the DOG by reaction with silver nitrate coated on Berl saddles. Iodine removal is satisfactory but the life of the bed in F-Area has been less than the design life. About half of the iodine which remains in the dissolver solution is subsequently released to the atmosphere through the process vessel vent system.

SUMMARY

Silver mordenite is a commercially available iodine adsorbent with potential advantages over the present silver nitrate coated Berl saddles in the adsorber bed. Silver mordenite is more stable chemically and thermally than silver nitrate on Berl saddles and has a higher capacity for iodine. Silver mordenite will increase bed life by a factor of 2 or 3, reduce waste volume, and lower the radiation exposure of workers who handle the waste. Silver mordenite could save about $13,500 per year now and $27,000 per year if two idine reactors are operating in the mid-80's. I recommend that silver mordenite be tested in the F-Area iodine reactor.

Iodine can be removed from the dissolver solution by sparging with air during the last half of the dissolution or by adding sodium nitrite solution. I recommend that SRP test air sparging (50 cubic feet per minute) and/or sodium nitrite addition in order to reduce ^{129}I emissions during routine operation and ^{131}I emissions if a green slug is accidentally dissolved.

USE OF SILVER MORDENITE IN IODINE REACTOR

Present Iodine Reactor

Porcelain Berl saddles coated with silver nitrate have been used to remove iodine from the DOG stream since plant startup. The iodine reactor in H-Area operates smoothly and is replaced infrequently ($\geq$5 years). The iodine reactor in F-Area has had many problems with pluggage which required removal of the cartridge or reactor.

The F-Area iodine reactor consists of a reactor shell into which a cartridge is inserted. The cartridge contains 20 cubic feet of 1/2inch Berl saddles coated with silver nitrate. The cylindrical cartridge is about 2 feet in diameter and is packed to a depth of 8 feet. The cartridge has an open top and a bottom perforated with 3/8-inch diameter holes. The DOG stream enters through two tubes at the top of the reactor. The stream is heated as it goes through tubes coiled around the cartridge and enters the cartridge from the bottom. The reactor is maintained at 178°C by high pressure steam in the reactor shell. This reactor was installed in 1964. Since 1964, 21 cartridges have been used with an average cartridge life of 9.1 $\pm$ 8.0 months and a median life of 6 months. One cartridge lasted one month and one cartridge lasted 30 months.[1,2]

Pluggage of the cartridge is due to two main problems: (1) entrainment of dissolver solution into the iodine reactor where the solution dries, depositing solids in the bottom of the cartridge and in the tubes leading to the cartridge; and (2) degradation of the Berl saddles to produce powdered material which settles to the bottom of the cartridge plugging the holes. Degradation is probably due to alternate exposure to base and acid vapors during decladding and dissolution cycles respectively. It is also possible to exceed the melting point of silver nitrate (212°C). The melted material seeps to the bottom of the cartridge and plugs the holes. Melting of silver nitrate has not been a problem since the operating temperature of the reactor was lowered from 191°C to 178°C.

Silver Mordenite

In order to improve the service life of the F-Area iodine reactor, I propose that silver mordenite be tested as a substitute for silver nitrate on Berl saddles. Silver mordenite offers improved chemical and thermal stability, lower waste volume, lower cost, and lower radiation exposure for workers. Table 1 shows characteristics of the two adsorbents.

Mordenite is a molecular sieve material with a silica/alumina mole ratio of 10/1 which gives the material good chemical and thermal stability.[3] Zeolon 900® extrudates have withstood 2000 hours reflux (103°C) in 6N HCl without destruction of either the pellet or the crystal structure.[3] In addition, mordenites have been shown to be stable in environments with pH as high as 12.[3] Thus, a silver mordenite with Zeolon 900® as the base material should be stable to the environment in the iodine reactor.

Silver mordenite is made by ion exchange of either the sodium or hydrogen form of Zeolon 900®. After exchange, the silver is reduced to the metallic state by heating in the presence of hydrogen.[4] Thus, no silver nitrate is present and there is no problem with melting as with silver nitrate because silver metal melts at 960°C. The reactor can be operated at higher temperatures if needed to ensure iodine removal.

Silver mordenite lowers the volume of waste produced because the silver concentration is much higher and, for a given amount of iodine removed, a smaller quantity of silver moredenite is required in the bed. Fully exchanged silver mordenite contains 19 weight percent silver compared to 3 weight percent silver on Berl saddles (see Table 1). In addition, more of the silver is available to react with iodine[4], probably because the higher surface area of the mordenite produces more reactive silver sites.

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Thus, 2.6 ft^3 of silver mordenite will collect as much iodine as the present 20 ft^3 full bed load of silver nitrate on Berl saddles. The smaller volume can be buried in a standard 30 gallon drum rather than the special 150 gallon container presently used to bury Berl saddles.

Lower costs are based on longer life of the silver mordenite bed, although a small savings is obtained even if the life is the same. Table 2 shows the costs considered and the savings realized. A two year life was assumed for the cartridge with silver mordenite. The costs per year for silver nitrate on Berl saddles were obtained by assuming a 9.1 month life. Thus, the cost per cartridge or change is multiplied by 1.32 to obtain the cost per year. The cost of adsorbent is based on plant cost including labor for silver nitrate on Berl saddles. The silver cost was $12 per ounce for the present adsorbent. The price for silver mordenite quoted by Ionex Corporation was adjusted to the same silver cost ($12 per ounce) rather than the present cost of $8.20 per ounce. A special waste container is used for burying Berl saddles at a cost estimated to be 25% more than the cost of an equivalent volume of 55 gallon steel drums. The silver mordenite requires one 30 gallon steel drum for burial. The cost savings shown is for one F-Area iodine reactor. When a second reactor is installed to handle the off-gas from the new annular dissolver, the savings will be doubled. The cost of labor and related overhead is not included because of the difficulty in estimating the labor savings. It is obvious that less time would be required to load or unload 150 pounds of adsorbent rather than 1200 pounds of adsorbent.

Exposure to radiation comes during loading and handling the waste container for burial. Radiation exposure is related to the time of exposure. Since it should take less time to load, seal, and remove a 30 gallon drum than a 150 gallon container the total radiation exposure should be less with the smaller waste volume.

Plant Test

Silver mordenite should be tested in the plant as a replacement for silver nitrate on Beryl saddles. The existing stack monitor can be used to determine that the release of iodine does not change during the test. If funds were available, it would be preferable to monitor iodine directly in the DOG. This more accurate measure of iodine is not required for a successful test.

To test silver mordenite, the bottom 24 inches of an existing cartridge should be packed with stainless steel wool to act as a demister. Silver mordenite (150 lbs of 1/8 inch extrudate) is placed on top of a No. 7 or 8 mesh screen. The initial pressure drop will be 5 to 10 inches of water column which is higher than with the Beryl saddles because of the particle smaller size of the mordenite. The reactor operating temperature should be in the range of 175 to 200°C. Silver mordenite can be purchased from Ionex Research Corporation, P. O. Box 602, Broomfield, CO 80020, phone (303) 535-4459. They list the material as Ionex Ag-900. It should be purchased in the reduced form.

REDUCTION OF IODINE RELEASES

When fuel is dissolved in F-Area only 40-50 percent of the iodine is evolved into the off-gas.[5] The remainder is spread through the system with some released to the stack via the process vessel vent system.[5] The releases result in >100 mCi of ^{129}I being released to the atmosphere each year.

These releases could be reduced by applying technology similar to that developed by Henrich, et al, or Johnson and Stone for LWR fuel reprocessing.[6,7,8] Henrich has demonstrated greater than 99% removal of radioactive iodine from simulated fuel solutions by sparging with NO_2 gas and addition of iodine compounds with natural isotopic abundance during the last half of the dissolution.[7] The NO_2 forms nitrous acid in solution. Nitrous acid reacts with ionic iodine species to yield elemental I_2 which can be sparged from solution. Sodium nitrite instead of NO_2 gas can easily be added to the dissolver solution to give nitrous acid and produce elemental iodine. As little as 50 ml of 30 wt% sodium nitrite solution should be adequate to reduce all iodine remaining in solution. Henrich added KIO_3 with natural abundance of iodine isotopes to maintain the iodine concentration at levels high enough for efficient stripping of iodine by sparging. Addition of KIO_3 does not seem necessary Johnson and Stone were able to strip >90% of the ^{129}I from dissolver solutions with only air sparging.[8] Their solutions had an equilibrium HNO_2 concentration of about 10^{-3}M due to radiolysis so addition of NO_2 was not necessary.

Based on the results above, I recommend that the plant test removal of iodine from dissolver solution by extending the present 50 cfm dissolver air sparge until the steam is turned off at the end of an acid cut. Analyses of dissolver solutions for ^{129}I with and without sparging would demonstrate how well air sparging alone works for iodine removal. If removal is inadequate, addition of $NaNO_2$ and KIO_3 can be tested to improve removal. The KIO_3 should be added prior to $NaNO_2$. Twenty-five grams of KIO_3 per 1000 liters of dissolver solution should be added in two equal portions. Each addition should be followed by a sodium nitrite addition and at least one hour of air sparging.

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TABLE 1

Comparison of Characteristics of Iodine Adsorbents

	$AgNO_3$/Berl Saddles	AgZ[a]
Volume of material, ft^3	20	2.6
Weight of material, lbs.	1200	150
Bulk density, lb/ft^3	60	57
Silver Content, wt%	3	19
Iodine loading, lb/lb adsorbent	0.007	0.10
Material size	1/2" saddles	1/8" extrudate
Bed height	98.5 in.	approx. 10 in.
Initial Pressure Drop, in. H_2O	3	5-10[b]
Frequency of replacement, months	9.1 ± 8.0[c]	24-30[d]
Volume of Waste, ft^3	>20	4[e]

[a]Silver mordenite
[b]Estimated on the basis of a minimum flow of 150 ft^3/min and a maximum flow of 400 ft^3/min.
[c]Statistical average and standard deviation for 21 cartridge changes.
[d]Based on replacement due to inefficiency.
[e]Assumes a 30 gallon waste drum for each cartridge change.

TABLE 2

Cost Savnings Per F-Area Iodine Reactor

	$AgNO_3$/Berl Saddles	AgZ
Cost of Adsorbent per Cartridge	$15,400	$14,175
Cost of Adsorbent per year	20,300	7,088
Cost of Waste Burial per Cartridge, $3/ft^3	60	12
Cost of Burial Container	150	14
Total Cost of Waste Burial per year	277	13
Total Cost per year	20,577	7,101
Cost Savings per year per reactor	$13,476	