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DU PONT

INTER-OFFICE MEMORANDUM

SAVANNAH RIVER PLANT

Key Words

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CHEMICAL RESISTIVITY OF SILVER MORDENITE AND BERL SADDLES

INTRODUCTION AND SUMMARY

The Separations Technology Laboratory was requested to determine the chemical resistance of pellets of silver mordenite and silver mordenite, reduced form. For comparison, Berl saddles were tested under similar conditions. Silver mordenite has been proposed (TA #2-1102) as a replacement for the saddles that remove iodine in the off-gas treatment system from the canyon dissolvers.

Submerged exposure to NaOH (19M or 2M) solutions at 85-100°C disintegrated both mordenite forms yielding small particulates from the pellets. Although the test length was some 2 hours, matrix degradation was noted shortly after reaching 85°C. After 2 hours at temperature, Berl saddles were notably attacked by 19M NaOH (50%), principally from caustic leaching and silver oxide precipitation, but they retained their structural integrity and form.

Similar exposure to distilled water or 14M HNO_3 (50%) produced varying degrees of attack to both mordenites and to the saddles. However, no structural deterioration occurred.

Both the mordenites and the Berl saddles contain SiO_2 and Al_2O_3 in their matrix structure. Analysis of the resulting acidic and caustic test solutions showed that the mordenite tests yielded about two orders of magnitude greater quantities (wt% of sample tested basis) of soluble aluminum than did the Berl saddles. For the water tests, the reverse was true, although the quantities solubilized were less than those produced by the acid or caustics.

EXPERIMENTAL

Samples Tested

Samples of both mordenite forms were in the shape of small cylinders approximately 3 mm diameter and from 5 to 12 mm in length. The silver mordenite contains silver as a salt, probably $AgNO_3$; the reduced mordenite contains silver as the metal. The reduced form is about 19 wt% silver. The matrix has a silica/alumina molar ratio of about 10/1.

The Berl saddles tested were from process stock and were roughly 15 mm in any dimension. The matrix silica/alumina molar ratio is about 6/1. They contain 3.8 wt% Ag in the form of $AgNO_3$.

Each sample of mordenite used for the tests weighed 2 ± 0.03 g. For each test, two Berl saddles, totaling between 5 and 6 g, were employed.

Test Conditions

All tests were conducted in the following manner. The solid sample was weighed and charged to a 1-liter, round-bottomed Pyrex® flask equipped with an immersion thermometer and a water-cooled Allihn condenser. To the flask was then added 100 mL of the test solution. The flask was heated with a hemispherical heating mantle, Variac-controlled. The flask and contents were slowly brought up to 100°C and maintained at that temperature (±5°C) for 2 hours. During the test, observations were noted. At the test conclusion, the flask contents were cooled. The liquid was drained from the flask. Recovered volumes were measured and were 98 mL, minimum. Samples of the liquid (and blanks) were submitted to H. M. Forrest of Laboratories for determination of the soluble silver and aluminum content via DCAP spectrometry.

OBSERVATIONS

Both forms of silver mordenite disintegrated to small, black particles shortly after reaching 85°C in the 19M NaOH solutions. The Berl saddles maintained their structure in 19M NaOH, although there was significant leaching of silver from the matrix as noted by the brownish-black silver oxide particulates produced in the solution. The reduced form of silver mordenite was also tested in 2M NaOH with very similar results. The particles formed, however, were slightly larger than those resulting from the 19M NaOH test.

Unreduced silver mordenite produced a dark amber color in the water solution test. Berl saddles gave a slight amber tint. The reduced silver mordenite gave an almost colorless solution.

The resulting test solids were darkened somewhat, but all maintained their structure.

The 14M HNO_3 tests gave essentially colorless solutions for all three solids. No structure deformation was noted. The particles were darkened by the test.

Polaroid photos, taken of some of the particles and the resulting test solutions, are attached on Page A-1. The dark solids in the caustic tests of the mordenites are the particulates resulting from disintegration of the samples. The bottom photo shows the Berl saddles before and after the 19M NaOH test. The solids noted in the solution from that test are silver oxide produced via leaching and precipitation.

RESULTS

Table 1, following, gives the total silver and aluminum contents of the various test solutions as determined by direct current argon plasma spectrometry, performed by H. M. Forrest, Laboratories.

TABLE 1

Ag & Al CONTENT OF SOLUTIONS EXPOSED TO MORDENITE & BERL SADDLES

	mg Element In 100 mL Solution Of			
	H_2O	14M HNO_3	19M NaOH	2M NaOH
Ag Mordenite*				
Ag	8	391	17**	-
Al	0.01	23	122**	-
Reduced Ag Mordenite*				
Ag	2	421	16**	16**
Al	0.01	25	109**	15**
Berl Saddles***				
Ag	100	101	16	-
Al	0.1	0.7	32	-

*2 g sample at 100°C for 2 hours

**Samples disintegrated

***5-6 g sample at 100°C for 2 hours

Since varying sample weights were employed, Table 2 presents this data normalized to weight percent of the original sample used. Therefore, a direct weight percent comparison, sample weight basis, can be made of the solubilized elements from the different tests.

TABLE 2

WT% Ag & Al, SAMPLE BASIS, IN TEST SOLUTIONS

	Element Wt%, Sample Basis, In 100 mL Of			
	H_2O	14M HNO_3	19M NaOH	2M NaOH
Ag Mordenite				
Ag	0.4	19.3	0.8*	-
Al	0.0005	1.1	6.0*	-
(Sample wt, g)	(2.007)	(2.024)	(2.022)	-
Reduced Ag Mordenite				
Ag	0.1	20.9	0.8*	0.8*
Al	0.0005	1.2	5.4*	0.7*
(Sample wt, g)	(2.017)	(2.012)	(2.006)	(2.028)
Berl Saddles				
Ag	2.0	1.8	0.3	-
Al	0.02	0.01	0.05	-
(Sample wt, g)	(5.040)	(5.725)	(5.988)	-

*Samples disintegrated

CONCLUSIONS

Examination of the data from Table 2 reveal that the mordenites consistently yielded approximately 100 times more soluble aluminum, per unit weight of sample, in the test solutions than did the Berl saddles, except for the water test case. Although less aluminum was produced in the 2M NaOH test of the reduced mordenite, it was still about fifteen times more, weight percent of sample basis, than the soluble Al produced by the 19M NaOH test of the Berl saddles. This comparison must also include the fact that the silica/alumina molar ratio in the mordenites is about 10; for the saddles, about 6. Therefore, the saddles, per unit weight, contain significantly more aluminum than do the mordenites. Soluble silica was not used as a comparative parameter since the tests were carried out in glass equipment.

Again except for the water case, three to ten times more soluble silver, weight percent of sample basis, was found for the mordenites versus that produced by the saddles. However, on a weight basis, the mordenites contain more silver than do the saddles.

One additional test was conducted. To ascertain if sintering might have a positive effect on the reduced mordenite's resistance to caustic, a small portion was heated to 700°C for 2 hours in a muffle furnace. A 2-gram sample of the heat-treated material exposed to 100 mL of 2M NaOH disintegrated while being heated between 85 and 100°C.

From their behavior in the tests and from the above data, it is concluded that the mordenites are not as structurally stable, vis-a-vis the saddles, and thus cannot withstand the corrosive chemical environment in the off-gas from the canyon dissolvers. Disintegration of the mordenites, caused by caustic conditions in the off-gas, would very likely lead to pluggage of the iodine reactor bed and, therefore, result in a high pressure drop across the cartridge containing the mordenites.

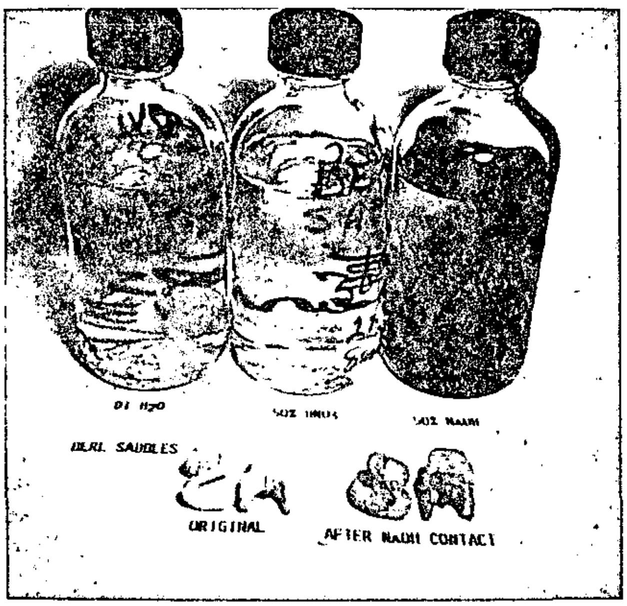
HPH/h

Attachment

PHOTOGRAPHS OF TEST SOLUTIONS AND SAMPLE MATERIALS

Test of Silver Mordenite

Test of Reduced Silver Mordenite



Test of Berl Saddles