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AUTHOR

L. L. Ames, Jr., R Fullerton

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U(VI) INCORPORATION DURING REPLACEMENT OF CALCITE BY ALKALINE, FLUORIDE-BEARING SOLUTIONS

L. L. Ames, Jr. and R. Fullerton[1]

HANFORD LABORATORIES OPERATION
General Electric Company
Richland, Washington

ABSTRACT

A mechanism involving oxygen in U(VI) incorporation operative during the metasomatic replacement of calcite by fluorite in alkaline, fluoride-bearing solutions was given further study. A Yates treatment of factorial design statistical data showed that temperature has a highly significant effect on the fraction of U(VI) removed from solution. An experimental comparison of oxygen-rich and oxygen- deficient influents demonstrated the existence of two mechanisms, the principal one involving oxygen, as originally postulated, probably as the substitution of $(UO_4)^{-2}$ for $(CaF_4)^{-2}$.

INTRODUCTION

In a previous paper the relationship between temperature and U(VI) substitutions during replacement of $CaCO_3$ by CaF_2 was discussed (1). It was hypothesized that U(VI) removal from solution during calcite replacement by fluorite in alkaline, fluoride-bearing solutions was related to the amount of oxygen dissolved in the replacing solution. Evidence for an incorporation mechanism involving oxygen was the inverse relationship between U(VI) removal from solution and temperature. It was concluded that the substitution might be that of the tetraoxouranate (VI) ion, or $(UO_4)^{-2}$, for CaF_4^{-2} (13), a mechanism that would account for the low temperature-uraniferous fluorite association reported by Gableman (4).

The proposed "oxygen" mechanism was investigated further by statistical design of experiments and data treatment. The results of this investigation are presented herein.

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METHODS OF INVESTIGATION

To treat the problem of the relationship between U(VI) removal from solution and temperature, a factorial design was devised (3). The six supposedly independent variables, U(VI) concentration, fluoride concentration, influent solution pH, system temperature, calcite surface area and column flow rate were studied at two levels utilizing the experimental apparatus of Figure 1. The fraction of U(VI) removed from solution was measured as the dependent variable by analysis of influent and effluent solutions. The composition of the influent solutions is given in Table I.

Table I. Composition of the influent solutions used in the factorial studies. All solutions were 1M NaCl in addition to their other constituents.

A) 0.01M NaF, 1.03×10^{-9}M U(VI) solution pH = 7.5	E) 0.05M NaF, 1.03×10^{-9}M U(VI) solution pH = 7.5
B) 0.01M NaF, 1.03×10^{-9}M U(VI) solution pH = 11.2	F) 0.05M NaF, 1.03×10^{-9}M U(VI) solution pH = 11.2
C) 0.01M NaF, 2.68×10^{-8}M U(VI) solution pH = 7.5	G) 0.05M NaF, 2.68×10^{-8}M U(VI) solution pH = 7.5
D) 0.01M NaF, 2.68×10^{-8}M U(VI) solution pH = 11.2	H) 0.05M NaF, 2.68×10^{-8}M U(VI) solution pH = 11.2

These eight solutions were used to complete a 2^6 factorial design in one half replicate (3). This design yields only main effects and two-factor interactions, with three-factor interactions used as an estimate of error. This design outline is shown in Figure 2. Calcite surface areas are inversely listed because calcite grain size designations, rather than surface areas, were used in these experiments.

Treatment of the analytical results on U(VI) removal from solution was by the method of Yates (3). Since only two levels were used, the t-test of significance could be utilized in gaging the relative importance of the effect totals at some level of t. Thus the design indicates whether the independent variables affect the dependent variable, and the relative order of their effect. The design does not show what the mechanism of U(VI) removal from solution is, or why it operates.

To substantiate the hypothesis that oxygen dissolved in the influent solution is associated with the removal of U(VI) from solution and incorporated into the fluorite lattice, calcite was allowed to react with fluoride ion under conditions similar to those previously reported (1). However, in one case 1M Na_2SO_3 was used in place of 1M NaCl, and the results were compared with U(VI) removal from the 1M NaCl solution. The Na_2SO_3 in solution effectively removed any dissolved oxygen but did not reduce the U(VI) to U(IV).

The appropriate sulfite-sulfate couple in basic solution (9) is

$$\begin{array}{lcl}
2OH^- + SO_3^{=} = SO_4^{=} + H_2O + 2e^- & & E^o = +0.930 \\
\underline{O_2 + 2H_2O + 4e^- = 4OH^-} & & \underline{E^o = +0.401} \\
2SO_3^{=} + O_2 = 2SO_4^{=} & & E^o = +1.331
\end{array}$$

A saturated solution at 25 C and one atmosphere would contain 0.0079g O_2/l, or 2.44×10^{-4}M O_2(7), as a reasonable approximation. Now $E = E^o - \frac{0.059}{n} \log_{10} Q$, where Q = the product of the activities of the resulting substances divided by the product of the activities of the reacting substances, n = the number of transferred electrons, and E^o = the standard electrode potential. Let us consider the reduction of oxygen in this system to barely detectable concentrations or $3.0 \times 10^{-6}\underline{M}$ O_2.

$$E = E^{\circ} - \frac{0.059}{4}\log_{10}\frac{(SO_4^{=})^2}{(SO_3^{=})^2(O_2)}$$

$$= +1.331 - \frac{0.059}{n}\log_{10}\frac{(4.88 \times 10^{-4})}{3.0 \times 10^{-6}}$$

$= +1.298$, the potential at quantitative O_2 removal.

These calculations show that all of the dissolved oxygen is removed from the influent solution. Furthermore, the experiment was carried out soon after solution makeup to prevent readsorption of oxygen from the atmosphere. Let us now calculate whether or not the U(VI) was reduced to U(IV). The applicable couples given by Latimer (9) are:

$$Na_2UO_4 + 4H_2O + 2e^- = U(OH)_4 - 2Na^+ + 4OH^- \qquad E^{\circ} = -1.61$$

$$2OH^- + SO_3^{=} = SO_4^{=} + H_2O + 2e^- \qquad E^{\circ} = +0.93$$

or combining

$$Na_2UO_4 + 3H_2O + SO_3^{=} = U(OH)_4 + 2Na^+ + 2OH^- + SO_4^{=} \quad E^{\circ} = -0.68$$

at pH 9:

$$E = -0.68 - \frac{0.059}{2}\log_{10}\frac{(Na^+)^2(OH^-)^2(SO_4^{=})}{(SO_3^{=})}$$

$$= -0.68 - \frac{0.059}{2}\log_{10}\frac{(1)^2(10^{-5})^2(4.88 \times 10^{-4})}{(1)}$$

$$= -0.29$$

Since the original oxygen concentration in the solution is approximately $2.44 \times 10^{-4}\underline{M}$, the sulfate concentration after reduction of all the oxygen would be twice this figure, or $4.88 \times 10^{-4}\underline{M}$. It is assumed in the calculation that solid Na_2UO_4 is the reacting species. In view of the low solubility of Na_2UO_4, and the mono- and polyuranates of the alkali metals in general (8), the assumption is probably valid.

Thus sulfite will not reduce U(VI) to U(IV). The stipulated environmental conditions were therefore fulfilled by substituting 1M Na_2SO_3 for 1M NaCl in the influent solution. Dissolved oxygen was removed effectively while U(VI) was not reduced to U(IV).

All chemicals used were of reagent grade in distilled water. Uranyl acetate was used as a source of U(VI). Uranium analyses were by the Analytical Laboratories of the Hanford Laboratories Operation.

RESULTS

Figure 3 gives the results of the factorial experiment in terms of the fraction of U(VI) retained by the forming fluorite for each of the independent variable conditions of Figure 2. Table II presents the effect totals and variance analysis of the data of Figure 3.

Table II. Analysis of variance of data from Figure 3.

Effect totals	Factor designation	Factors	Effect totals	Factor designation	Factors
16.6936					
1.4738	a	Calcite surface area	2.2438	a	Fluoride concentration
1.3720	b	Column flow rate	-.7280	ae	
.4062	ab		-.4642	be	
-1.1422	c	U(VI) concentration	1.5988	abe	(error)
.0552	ac		.6600	ce	
1.3774	bc		.9614	ace	(error)
.9248	abc	(error)	.4332	bce	(error)
1.2330	d	Influent solution pH	1.0654	abce =	df
.7864	ad		.5892	ce	
-1.4750	bd		1.1210	ade	(error)
- .1860	abd	(error)	.2548	bde	(error)
1.4680	cd		-.8458	abde =	ce
1.8308	acd	(error)	.0922	cde	(error)
-.4580	bcd	(error)	.9246	acde =	bf
.2466	abcd =	ef	-.7402	bcde =	af
			5.7060	abcde =	f Temperature

(continued)

$$
\begin{aligned}
\sigma^2 &= 0.0295 \\
\sigma &= \pm 0.1718 \\
\sigma_{\text{Effect total}} &= (\sqrt{32})\,(0.1718) \\
&= \pm 0.9718 \\
t &= 3.169, \text{ for the 99 percent confidence level and ten degrees of freedom.} \\
(0.9718)(3.169) &= \pm 3.0796
\end{aligned}
$$

An effect total is significant at the 99 percent level if greater than ± 3.0796. At a lower level - such as 95 percent - the F^- concentration, as well as the temperature, would be significant.

Note that there is only one significant effect at the 99 percent level of t under these experimental conditions and that effect is for temperature. In other words, with greater than 99 percent certainty, it can be stated that temperature has a real effect on U(VI) removal. A simple visual examination of the independent variables of Figure 3 shows that this temperature effect is an inverse one, i.e., all other things being equal, the higher the temperature the less U(VI) removed from solution. Thus the original data (1), indicating an inverse U(VI) removal-temperature relationship, was correct with a high degree of probability.

Figure 4 compares the results of the 1<u>M</u> NaCl and 1<u>M</u> Na_2SO_3 experiments. Note two removal curves, indicating two removal mechanisms. The effect of the "oxygen" mechanism is pronounced at low temperatures. for example, at 25° C 88.4 percent of the U(VI) removed can be attributed to the "oxygen" removal mechanism.

An experiment utilizing 0.3<u>M</u> Na_2SO_3, rather than 1<u>M</u> Na_2SO_3, to duplicate the ionic strength of the 1<u>M</u> NaCl influent yielded U(VI) removals not significantly different than U(VI) removals from the original 1<u>M</u> Na_2SO_3 solution.

DISCUSSION

Analysis of the factorial data demonstrated that the earlier postulated inverse relationship between U(VI) removal and temperature actually existed. The relationship of U(VI) removal to temperature and oxygen content was also shown by comparing the results of two experiments, one solution containing dissolved oxygen and the other containing little or no dissolved oxygen.

There are apparently two mechanisms operative in removal of U(VI) during the replacement of calcite by fluorite. In the absence of dissolved oxygen, the "normal" mechanism operates, probably by substitution of $(UO_2)^{+2}$ for $(2CaF)^{+2}$ as postulated previously (2). This "normal" mechanism operated under all conditions during replacement of calcite by apatite; i.e., oxygen did not affect U(VI) removal during the replacement of calcite by apatite. An alternative explanation of the shape of the U(VI) removal curve from 1M Na_2SO_3, is the formation of U(VI) sulfite complexes. Although such complexes are alluded to in the literature, no stability data were found. Therefore this possibility cannot be evaluated at present. The second, or "oxygen" mechanism, is restricted to the calcite-fluoride replacement reaction (1) and is probably represented by the substitution of $(UO_4)^{-2}$ for $(CaF_4)^{-2}$ (13).

The U(VI) removal curve labeled "1M NaCl" in Figure 4 represents the sum of the "normal" mechanism plus the "oxygen" mechanism. The curve labeled "1M Na_2SO_3" represents the effect of the "normal" mechanism only. At one atmosphere of pressure, the effect of increasing the solution temperature is deoxygenation of the solution. Increasing the partial pressure of oxygen would tend to shift both of the curves shown in Figure 4 to the right, assuming that U(VI) removal rates for the normal mechanism continue to increase with rising temperature. Hence, there is probably little change in curve relationships between one atmosphere oxygen partial pressure at lower temperatures and several atmospheres at higher temperatures.

All other things being equal, the lower temperature fluorite deposits would tend to be uranium-rich as reported by Gabelman (4). The uranium would be disseminated through the fluorite lattice. The field occurrences of such fluorite deposits (5, 6, 10, 11 and 12) parallel the general relationships between U(VI) ion, temperature and resulting U(VI) removal from solution as determined in the laboratory.

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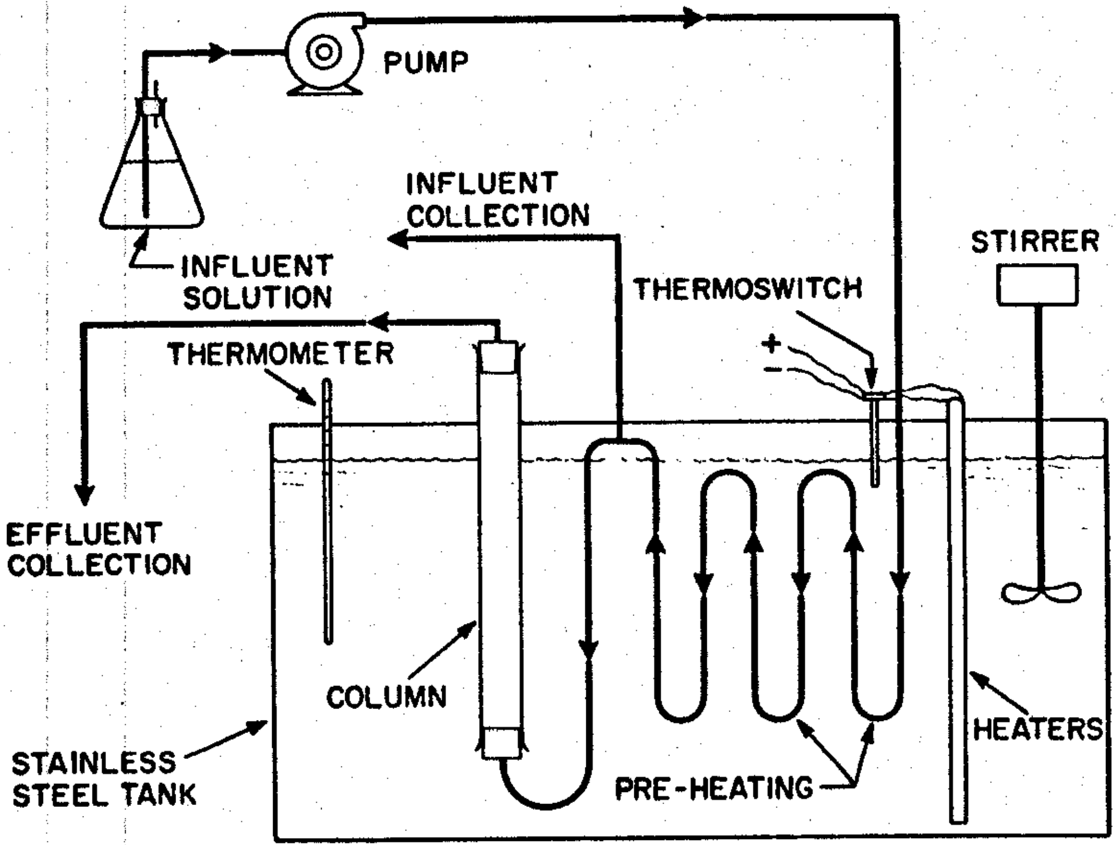

Fig. 1. Experimental apparatus.

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			INFLUENT pH 7.5				11.2			
			FLUORIDE CONCENTRATION 0.01 M		0.05 M		0.01 M		0.05 M	
FLOW RATE	CALCITE SURFACE AREA	U (VI) CONCENTRATION	TEMPERATURE 25 °C	60 °C	25 °C	60 °C	25 °C	60 °C	25 °C	60 °C
294 ml/cm^2/hr	0.121 m^2/g	1.03×10^{-9} M	SOLUTION B			SOLUTION F		SOLUTION A	SOLUTION E	
		2.68×10^{-8} M		SOLUTION D	SOLUTION H		SOLUTION C			SOLUTION G
	0.032 m^2/g	1.03×10^{-9} M		SOLUTION B	SOLUTION F		SOLUTION A			SOLUTION E
		2.68×10^{-8} M	SOLUTION D			SOLUTION H		SOLUTION C	SOLUTION G	
850 ml/cm^2/hr	0.121 m^2/g	1.03×10^{-9} M		SOLUTION B	SOLUTION F		SOLUTION A			SOLUTION E
		2.68×10^{-8} M	SOLUTION D			SOLUTION H		SOLUTION C	SOLUTION G	
	0.032 m^2/g	1.03×10^{-9} M	SOLUTION B			SOLUTION F		SOLUTION A	SOLUTION E	
		2.68×10^{-8} M		SOLUTION D	SOLUTION H		SOLUTION C			SOLUTION G

Fig. 2. The experimental design under which the solutions of Table I were utilized.

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FLOW RATE	CALCITE SURFACE AREA	U (VI) CONCENTRATION	INFLUENT pH 7.5				11.2			
			FLUORIDE CONCENTRATION 0.01 M		0.05 M		0.01 M		0.05 M	
			TEMPERATURE 25 °C	60 °C	25 °C	60 °C	25 °C	60 °C	25 °C	60 °C
294 $ml/cm^2/hr$	0.121 m^2/g	1.03×10^{-9} M	0.9200			0.0009		0.3800	0.7111	
		2.68×10^{-8} M		0.7143	0.8000		0.8333			0.0769
	0.032 m^2/g	1.03×10^{-9} M		0.2903	0.4934		0.7667			0.3333
		2.68×10^{-8} M	0.6667			0.4211		0.3667	0.6154	
850 $ml/cm^2/hr$	0.121 m^2/g	1.03×10^{-9} M		0.2000	0.7467		0.5800			0.0010
		2.68×10^{-8} M	0.8857			0.5790		0.3333	0.5770	
	0.032 m^2/g	1.03×10^{-9} M	0.4667			0.3643		0.3333	0.4944	
		2.68×10^{-8} M		0.4048	0.3158		0.6333			0.0010

Fig. 3. Fraction of U(VI) retained on a fifty-gram column of calcite under the listed experimental conditions. All solutions contained 1M NaCl in addition to the above-listed constituents.

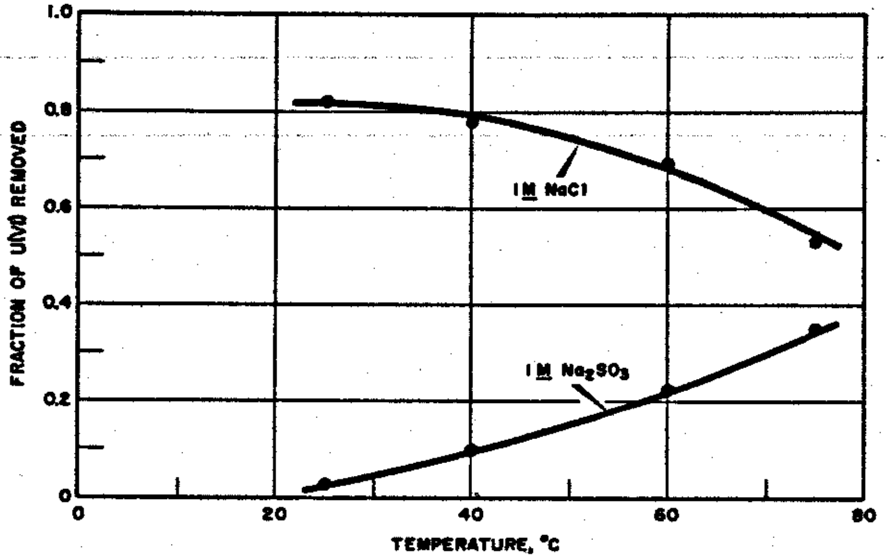

Fig. 4. The removal of U(VI) during the replacement of calcite by fluorite under oxidizing and reducing conditions.

	1M NaCl solution	1M Na_2SO_3 solution
Influent composition	1.35x10^{-8}M U(VI), 0.05M NaF, 1M NaCl	2.68x10^{-8}M U(VI), 0.05M NaF, 1M NaCl
Influent pH	9.0	9.8
Influent temperature	40° C	40° C
Column flow rate	410 ml/cm^2/hr	410 ml/cm^2/hr
Calcite surface area	0.067 m^2/g	0.067 m^2/g
Column	50g calcite	50g calcite
System pressure	one atmosphere	one atmosphere