DEVELOPMENT OF AN α - EMITTING WASTES IMMOBILIZATION TECHNIQUE USING URANIUM CHROMITE MATRICES WITH ADDED BASALT-LIKE MATERIALS

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ABSTRACT

The results of studies of an immobilization method for elements in radioactive wastes represented by uranium are presented. The method was based on the immobilization of uranium as uranium chromite. However, taking into account its high melting and sintering temperatures, we designed a method of forming uranium chromite monoliths by introducing of basalt or sinthetic basalt. These additions not only reduce the sintering temperature but also decrease the leaching rate of the composite.

INTRODUCTION

Previously, it was shown that uranium chromite, uranium niobate and their mixtures must be sintered at high temperature (e.g., 1350 to 1450° C for mixtures of uranium chromite with 5 to 7.5 wt. % uranium niobate) to obtain a high-density matrix (pellets and blocks) and to allow incorporation of rare earth elements (REE) and transplutonium elements (TPE) in the matrix. The ability to decrease the sintering temperature of such mixtures by adding readely fusing basalt-like dopants to the mixtures was studied. A secondary purpose of these studies was to increase the hydrolytic stability of the resulting matrices (i.e. decrease radionuclide leach rate from particles of the material immersed in water). The method used to reduce leachability was to create an additional protective barrier by adding a non-radioactive, chemically stable layer of melted glassy-crystalline or glassy basalt-like materials to the uranium chromite particles. Uranium chromite mixtures with basalt or basalt simulant, with and without added B_2O_3, were investigated.

Uranium chromite powder, as a model matrix for immobilization of TPE and REE in radioactive wastes, was prepared from titrated solutions of uranyl nitrate and chromium nitrate (or chromic acid) by mixing them in equimolar quantities. The resulting uranium - chromium solutions were evaporated and sintered at 1000° C for 1 hour. The resulting solids were powdered and the fraction less then 0.2 mm was separated out. Basalt and synthetic basalt were powdered in a mortar, the fraction less then 0.2 mm was collected and then ground in a ball vibromill.

Powders of uranium chromite and basalt or synthetic basalt were mixed in the necessary weight proportions and further ground in a vibromill. The resulting powders were pelletized (pellet diameters were 7 to 8 mm and heights were 5-to 10 mm) by cold pressing at pressures up 1 to 7 t/cm^2. As necessary a binder was addied, consisting of a solution of 60 mg of paraffin in 2 ml heptane per on 3 g of the powders mixture. The heptane was removed by drying before cold pressing of pellets.

The influence of the powders mixture composition and the preparation and consolidation (pelletization and sintering) conditions on (the density, form, and leach rates of the sintered pellets) has been studied. The leach rates were studied by placing pellets in twice-distillate water. The results are shown in Tables I-IV.

SINTERING OF MIXTURES AND PROPERTIES OF SINTERED PELLETS

It was impossible to obtain durable pellets from uranium chromite +basalt or uranium chromite + synthetic basalt sintered at 1000^o C for all studied compositions from 10 to 90 wt. % uranium chromite. However, good, durable pellets resulted for all these compositions when the sintering temperature was increased. The sintering time was 1 hour for all experiments.

Table I. Cromite U : basalt system. The influence of composition and T sintering

composition, % wt.			Pressure	T sintering,°C, $\tau = 1$ hour	Specific density, ρ, g/cm^3	Surface, S, cm^2	The time of leaching, τ, day.	The rate of leaching,- g/(cm^2.day)					
Chromite U	Basalt	B_2O_3	$P_{sp.}$, t/cm^2					Cr	Mg	Ca	Si	B	Fe
10	90	–	4.0	1000	2.22	–	–	–	–	–	–	–	–
				1100	2.29	3.34	17	$<1\times10^{-7}$	1.1×10^{-5}	7.3×10^{-6}	1.0×10^{-6}	–	1.1×10^{-7}
20	80	–	4.0	1000	2.35	–	–	–	–	–	–	–	–
				1100	2.44	2.86	17	$<1\times10^{-7}$	9.0×10^{-6}	6.7×10^{-6}	1.3×10^{-6}	–	1.4×10^{-7}
30	70	–	4.0	1000	2.49	–	–	–	–	–	–	–	–
				1100	2.61	2.86	17	$<1\times10^{-7}$	1.2×10^{-5}	6.0×10^{-6}	1.2×10^{-6}	–	1.3×10^{-7}
40	60	–	4.0	1000	2.64	–	–	–	–	–	–	–	–
				1100	2.86	2.72	17	$<1\times10^{-7}$	1.2×10^{-5}	–	1.2×10^{-6}	–	1.0×10^{-7}
50	50	–	4.0	1100	2.98	3.25	17	$<1\times10^{-7}$	1.1×10^{-5}	5.0×10^{-6}	1.4×10^{-6}	–	1.4×10^{-7}
60	40	–	4.0	1100	3.23	3.35	17	$<1\times10^{-7}$	2.0×10^{-5}	8.0×10^{-6}	2.7×10^{-6}	–	2.1×10^{-7}
70	30	–	4.0	1100	3.67	3.31	11	$<3\times10^{-8}$	5.1×10^{-6}	6.8×10^{-6}	7.0x10-6	-	6.9×10^{-8}
80	20	–	4.0	1100	3.69	2.67	36	$<1\times10^{-8}$	1.5×10^{-5}	7.8×10^{-6}	7.4×10^{-6}	–	1.8×10^{-7}
90	10	–	1.0	1000	3.74	–							
				1100	3.88	2.80	36	$<1\times10^{-8}$	2.1×10^{-5}	2.2×10^{-5}	8.9×10^{-6}	–	9.6×10^{-8}
50	50	–	4.0	1000	2.78	–	–	–	–	–	–	–	–
				1100	2.93	3.62	26	$<1\times10^{-7}$	8.3×10^{-6}	–	1.8×10^{-6}	–	$<1\times10^{-8}$
60	40	–	4.0	1350	3.84	2.45	28	$<8\times10^{-9}$	3.9×10^{-7}	3.7×10^{-7}	3.7×10^{-7}	–	$<2\times10^{-8}$
70	30	–	4.0	1350	4.54	2.77	28	$<6\times10^{-9}$	1.7×10^{-7}	1.7×10^{-7}	1.2×10^{-6}	–	$<2\times10^{-8}$
90	10	–	1.0	1350	5.22	2.50	28	$<6\times10^{-9}$	9.1×10^{-7}	6.7×10^{-6}	2.2×10^{-6}	–	$<7\times10^{-8}$

Table II. Uranium chromite : rock casting system. The influence of composition and T sintering

composition, % wt.			Pressure	T sintering,°C, τ = 1 hour	Specific density, ρ, g/cm^3	Surface, S, cm^2	The time of leaching, τ, day.	The rate of leaching,- g/(cm^2.day)					
Chromite U	Rock casting	B_2O_3	P_{sp} ,t/cm^2					Cr	Mg	Ca	Si	B	Fe
10	90	–	1.0	1000 1100	2.23 2.38	– 2.91	– 15	– $<1\times10^{-7}$	– 3.1×10^{-6}	– 3.0×10^{-6}	– 1.1×10^{-6}	– –	– 1.3×10^{-7}
30	70	–	1.0	1000 1100	2.43 2.62	– 3.35	– 15	– $<1\times10^{-7}$	– 4.4×10^{-6}	– 4.7×10^{-6}	– 1.2×10^{-6}	– –	– 1.2×10^{-7}
50	50	–	1.0	1000 1100	2.77 2.95	– 2.61	– 15	– $<1\times10^{-7}$	– 7.1×10^{-6}	– 6.7×10^{-6}	– 1.4×10^{-6}	– –	– 2.1×10^{-7}
60	40	–	1.0	1000 1100	2.93 3.14	– 2.38	– 15	– $<1\times10^{-7}$	– 9.6×10^{-6}	– 9.8×10^{-6}	2.6×10^{-6}	– –	– 2.6×10^{-7}
70	30	–	1.0	1000 1100	3.50 3.73	– 2.25	– 23	– 6.2×10^{-8}	– 1.3×10^{-5}	– 1.4×10^{-5}	– 4.4×10^{-6}	– –	– 3.6×10^{-7}
80	20	–	1.0	1000 1100	3.34 3.43	– 2.40	– 35	– 5.8×10^{-8}	– 1.1×10^{-5}	– 1.6×10^{-5}	– 1.3×10^{-5}	– –	– 2.5×10^{-7}
90	10	–	1.0	1000 1100	3.77 3.81	– 2.27	– 35	– $<1\times10^{-8}$	– 2.7×10^{-5}	– 2.1×10^{-5}	– 2.8×10^{-5}	– –	– 4.7×10^{-7}
80	20	–	3.0	1000	3.64	3.01	26	$<1\times10^{-7}$	2.0×10^{-5}	7.8×10^{-6}	5.7×10^{-6}	–	$<3\times10^{-8}$
80	20	–	3.0	1100	3.96	2.99	26	$<1\times10^{-7}$	2.1×10^{-5}	1.3×10^{-6}	6.5×10^{-6}	–	$<3\times10^{-8}$
80	20	–	3.0	1200	4.73	2.33	28	$<1\times10^{-7}$	1.7×10^{-6}	5.6×10^{-6}	10.0×10^{-6}	–	$<4\times10^{-8}$
80 80	20 20	– –	3.0 2.0	1300 1300	4.86 4.76	2.31 2.96	28 28	$<5\times10^{-9}$ $<5\times10^{-9}$	1.5×10^{-6} 1.3×10^{-6}	6.6×10^{-6} 2.1×10^{-6}	3.4×10^{-7} 1.4×10^{-6}	– –	$<3\times10^{-8}$ $<3\times10^{-8}$
90	10	–	3.0	1000	3.90	2.83	26	$<1\times10^{-7}$	2.3×10^{-5}	8.6×10^{-6}	5.1×10^{-6}	–	$<7\times10^{-8}$
90	10	–	3.0	1100	3.92	2.97	26	$<1\times10^{-8}$	2.8×10^{-5}	1.7×10^{-5}	9.1×10^{-6}	–	$<7\times10^{-8}$
90	10	–	2.0	1200	4.30	3.01	28	$<1\times10^{-8}$	1.2×10^{-5}	3.0×10^{-5}	1.2×10^{-5}	–	$<7\times10^{-8}$
90	10	–	2.0	1300	4.88	2.44	28	$<1\times10^{-8}$	3.5×10^{-6}	1.5×10^{-5}	5.0×10^{-6}	–	$<7\times10^{-8}$

Table III. Uranium chromite – basalt (melt with B_2O_3) system, grinding and vibromill. Influence of composition and T sintering

composition, % wt.			Pressure	T sintering, °C, τ = 1 hour	Specific density, ρ, g/cm^3	Surface, S, cm^2	The time of leaching, τ, day.	The rate of leaching,- g/(cm^2.day)					
Chromite U	Basalt	B_2O_3	P_{sp} ,t/cm^2					Cr	Mg	Ca	Si	B	Fe
90	8.5	1.5	2.0	1100 1000	4.34 3.90	2.76 –	28 –	$<5\times10^{-9}$ –	1.4×10^{-5} –	– –	7.7×10^{-6} –	1.3×10^{-5} –	– –
80	17	3.0	1.5	1100 1000	4.30 3.93	2.66 –	28 –	$<6\times10^{-9}$ –	 –	5.1×10^{-6} –	1.0×10^{-6} –	8.0×10^{-7} –	– –
70	25.5	4.5	2.0	1100 1000	3.51 3.69	3.12 –	28 –	$<6\times10^{-9}$ –	9.3×10^{-7} –	3.1×10^{-6} –	1.2×10^{-6} –	1.9×10^{-7} –	– –
60	34	6.0	3.0	1100 1000	3.19 3.33	3.20 –	28 –	1×10^{-8} –	 –	7.3×10^{-7} –	1.6×10^{-7} –	3.3×10^{-8} –	– –
50	42.5	7.5	4.0	1100 1000	~ 2.90 2.61	2.01 –	28 –	$<1\times10^{-8}$ –	4.9×10^{-7} –	1.4×10^{-6} –	3.2×10^{-7} –	1.1×10^{-7} –	– –
80	17	3.0	2.0	1350	4.64	2.17	28	$<7\times10^{-9}$		2.0×10^{-6}	3.4×10^{-7}	1.8×10^{-7}	–
70	25.5	4.5	4.0	1350	3.46	2.72	28	$<7\times10^{-9}$	1.9×10^{-7}	1.7×10^{-6}	2.2×10^{-7}	$<3\times10^{-8}$	–
60	34	6.0	3.0	1350	3.02	2.99	28	$<7\times10^{-9}$		2.1×10^{-6}	6.8×10^{-7}	$<3\times10^{-8}$	–
50	42.5	7.5	4.0	1350	2.640	3.42	28	$<7\times10^{-9}$	2.4×10^{-7}	1.1×10^{-6}	1.0×10^{-7}	2×10^{-8}	–

Table IV. Uranium chromite – rock casting system, melt with B_2O_3 15%, grinding and vibromill. Influence of composition and T sintering

composition, % wt.			Pressure	T sintering,°C, τ = 1 hour	Specific density, ρ, g/cm^3	Surface, S, cm^2	The time of leaching, τ, day.	The rate of leaching,- $g/(cm^2.day)$					
Chromite U	Rock casting	B_2O_3	P_{sp}, t/cm^2					Cr	Mg	Ca	Si	B	Fe
50	42.5	7.5	1.0	1000	3.10		–	–	–	–	–	–	–
60	34	6.0	1.0	1000	3.17		–	–	–	–	–	–	–
70	25.5	4.5	1.0	1000	3.31		–	–	–	–	–	–	–
80	17	3.0	1.0	1000	3.54		–	–	–	–	–	–	–
90	8.5	1.5	1.1	1000	3.83		–	–	–	–	–	–	–
50	42.5	7.5	1.0	1100	3.22	3.25	28	$<8\times10^{-9}$	2.5×10^{-7}	7.3×10^{-7}	2.5×10^{-7}	1.0×10^{-7}	–
60	34	6.0	1.0	1100	3.30	3.12	28	$<7\times10^{-9}$		1.3×10^{-6}	2.4×10^{-7}	1.0×10^{-7}	–
70	25.5	4.5	1.0	1100	3.61	2.73	28	$<6\times10^{-9}$	8.1×10^{-7}	3.6×10^{-6}	1.9×10^{-6}	6.0×10^{-7}	–
80	17	3.0	1.0	1100	3.88	2.21	28	$<7\times10^{-9}$	1.4×10^{-6}	1.3×10^{-5}	4.0×10^{-6}	2.7×10^{-6}	
90	8.5	1.5	1.0	1100	4.06	2.65	28	6.7×10^{-7}	1.3×10^{-5}	1.4×10^{-5}	1.2×10^{-5}	1.2×10^{-5}	
50	42.5	7.5	3.0	1200	2.82	3.46	28	$<7\times10^{-9}$	1.3×10^{-7}	1.2×10^{-6}	2.6×10^{-7}	1.3×10^{-7}	
60	34	6.0	3.0	1200	3.30	2.98	28	$<7\times10^{-9}$		1.7×10^{-6}	6.1×10^{-7}	2.8×10^{-7}	
70	25.5	4.5	3.0	1200	3.65		–	–	–	–	–	–	–
80	17	3.0	3.0	1200	4.10		–	–	–	–	–	–	–
50	42.5	7.5	3.0	1300	–	–	–	–	–	–	–	–	–
60	34	6.0	3.0	1300	–	–	–	–	–	–	–	–	–
70	25.5	4.5	3.0	1300	3.66	3.29	28	$<5\times10^{-9}$	3.5×10^{-7}	9.5×10^{-7}	2.4×10^{-7}	1.2×10^{-7}	
80	17	3.0	3.0	1300	4.19	3.12	28	$<5\times10^{-9}$	8.8×10^{-7}	3.4×10^{-6}	1.7×10^{-6}	6.0×10^{-7}	
90	8.5	1.5	3.0	1300	4.77	2.66	28	$<5\times10^{-9}$	8.4×10^{-6}	2.5×10^{-6}	4.5×10^{-6}	2.3×10^{-6}	

As the sintering temperature was increased to 1300-1350° C pellets with a low uranium chromite content sintered better, although some were still hard to sinter and melted. At high uranium chromite content (80-90 wt.%) pellets did not melt even at 1300-1350° C (see tables I and II).

Durable pellets were prepared when mixtures of uranium chromite, basalt or synthetic basalt and B_2O_3 (15 wt. %) were consolidated by heating at only 900-1000° C. A trace of pellets fusing was detected when the uranium chromite content was only 10-50 wt.% at 1000° C, and when the temperature was increased to 1100° C - pellets containing only 10-30 wt. % uranium chromite melted.

Durable pellets without a trace of fusing at 1000° C resulted when a powdered mixture of basalt or synthetic basalt that had been previously melted with B_2O_3 was used in the pellet forming process. These pellets did not melted at uranium chromite contents -of up to 80-90%-, and temperatures of up to 1300-1350° C.

The influence of unit pressure on the strength and density of sintered pellets of uranium chromite mixed with basalt and synthetic basalt.

It was shown that at pressures of from 1-5 t/cm^2 the density of pellets sintered at 1000-1100° C increases slightly as the pressure increases 6 to 7 % (as does the density of non-sintered pellets). A further increase in pressure -to 7 t/cm^2- brings about repelletization and the pellets crack or break up before sintering.

The influence of composition and sintering temperature on pellets density.

In the most thoroughly studied systems the density of pellets sintered at 1000-1100° C was determined to depend on the uranium chromite content. From this data it is clear that when the uranium chromite content and sintering temperature increase the pellets density increases. When the uranium chromite content increases from 10 to 90 wt. % the sintered pellet density increases from 2.2 to 3.7-3.8 g/cm^3 at 1000° C and from 2.3-2.4 to 3.7-4.3 g/cm^3 at 1100° C in most cases.

The influence of temperature on the density of sintered pellet was investigated specifically for high uranium chromite content systems. The data obtained for different compositions are given in tables I-IV.

As seen from the data, the pellet density increases from 3.7 to 4.9 g/cm^3 when the sintering temperature increases from 1000 to 1300° C for mixtures of 80 wt. % uranium chromite and basalt or synthetic basalt. The pellets density decreased slightly upon introduction of 15 wt. % B_2O_3 to the basalt or synthetic basalt i.e., 3.5-4.2 g/cm^3 at 1000 to 1350° C.

The density of pellets containing 90 wt. % uranium chromite that were sintered at 1000 to 1350° C was increased from 3.8 to 5.2 g/cm^3. Pellets with maximal density were obtained from the chromite-basalt systems including those with B_2O_3 added. The maximum density achieved for sintered pellets was 5.2 g/cm^3; this was ~62% of the theoretical density for pure uranium chromite (8.3 g/cm^3).

Aqueous leach rate of pellets made with mixtures of uranium chromite and basalt or synthetic basalt

This section provides the results of measuring of aqueous leach rate of uranium chromite-based pellets, specifically the dependence of the leach rates of major elements on the amounts of basalt or synthetic basalt in the pellet as well as other factors including sintering temperature and the amount of boron added.

Uranium chromite : basalt systems.

The results showing the influence of the uranium chromite: basalt system composition on the rate of leaching of Cr, Mg, Ca, Si and Fe are given in table I. In pellets, sintered at 1100° C and above, the leach rate of chromium was less than 1×10^{-7} g/(cm^2.day), for uranium chromite content from 10 to 90 wt. %. This indicates that uranium chromite does not dissolve in twice-distilled water in spite of its being sintered with different amounts of basalt. More accurate rates of Cr leaching would likely be obtained for longer leaching times.

Varying the pellet composition did not appreciably change the Mg, or Fe leach rates ~10^{-5} and 10^{-7} g/(cm^2 day), respectively.

The Ca and Si leach rates did not vary for uranium chromite content of 10-to 80 wt. %, but at 90 wt. % the leach rates for these elements increased by up to a factor of three under some of the test conditions.

The leach rate of all analyzable elements decreased, when the sintering temperature increased from 1100° C to 1350° C for pellets with a high uranium chromite content (60-90 wt. %) apparently due to an interaction of the insoluble uranium chromite with the basalt. For example, Mg and Ca leach rates decreased by factors of multiples of ten; Fe, by factor of 10; and Si, by several fold. This assumption will be checked on future work.

The dependence of element leach rates on the pellet sintering temperature is given in table I. The leach rate of all elements decreased considerably when the sintering temperature was increased from 1000° C to 1350° C. For example, the Mg leach rate for pellets containing 80-90 wt. % uranium chromite decreased by factor of 15 to 50, when the sintering temperature was increased from 1000° C to 1300-1350° C, respectively. Under this conditions the Ca leach rate (for both compositions) decreased by a factor of ~3; the Si, leach rate decreased by factors of 6 to 10.

Uranium chromite : synthetic basalt systems.

The data showing the influence of uranium chromite: synthetic basalt system composition and sintering temperature on the rate of leaching for several elements are given in table II. The leach rate of Cr was less than 1×10^{-7} g/(cm^2 day); that for Mg and Fe - increased 10 and 5 times, respectively, when the uranium chromite content increased from 10 to 90 wt. % in the synthetic basalt-based mixture. The leach rate of Ca and Si did not change when the uranium chromite content increased to 60 wt. %, but increased by a factor of 7 for Ca and 25 for Si when the uranium chromite content increased from 60 to 90 wt. %.

From the data in tables I and II the following conclusion are apparent:.

The leach rate of certain elements, e.g. Ca and Si, increases appreciably in the systems with high uranium chromite content. The leach rate of Mg in the uranium chromite - basalt system with low uranium chromite content is higher than that in the uranium chromite – synthetic basalt system with similar uranium chromite content. The leach rates of Si and Fe for the uranium chromite : basalt and synthetic basalt systems at < 70 wt. % uranium chromite are similar. It is hoped that further detailed investigation will illuminate the cause of the difference in the rates of leaching of certain other elements from the basalt and from the synthetic basalt-based systems.

The results of investigation of the influence of sintering temperature on the leach rate for mixtures of both 80 and 90 wt. % uranium chromite + synthetic basalt are given in table II. Essentially, a decrease in the leach rates of Mg, Ca and Si was observed for both compositions as the sintering temperature increased from 1000° C to 1300° C. In general for this system, the leach rate for these elements were similar for the different composition pellets sintered at a given temperature. For the 90 wt. % uranium chromite : synthetic basalt system, however, an increase of sintering temperature from 1000° C to 1300° C decreased only the leach rate for Mg (by a factor of~ 6). This is in contrast to the 90 wt. % uranium chromite : basalt system, where the leach rates for both Ca and Mg were decreased, under the same conditions, and to the remaining results for the uranium chromite : synthetic basalt system, where the rate of leaching was not changed very mach when the sintering temperature was increased. Further special investigation would be needed to explain this difference in behavior. The Fe leach rate was less then 1×10^{-7} g/(cm^2 day) for all uranium chromite: synthetic basalt pellets for the range of sintered temperatures studied. Different results might be obtained for longer leach times. It also stands to reason that the determining the rate of leaching of Mg, Ca, Fe and other base elements from these matrices will not necessarily yield information on leach rates of the radionuclides of interest and on the suitability of these matrices for immobilizing radioactive wastes. The leaching studies do, however, yield information that can be used in predicting the chemical stability of the matrices and to facilitate predictions of the behavior of radionuclides such as Sr, REE and TPE incorporated in the matrix; as a rule, these radionuclides are more strongly held in such matrices than Ca. Further studies are planned to evaluate the leaching behavior of Cs, Sr, REE and TPE in these systems.

Uranium chromite : basalt, or synthetic basalt + boron systems.
Uranium chromite : basalt, or synthetic basalt systems doped with boron have been investigated. The method of boron introduction was varied.

Uranium chromite: synthetic basalt + B_2O_3 systems.
In this section leach rates of pellets made from uranium chromite powder - mixed with powdered synthetic basalt previously melted with B_2O_3 are discussed. Powdered synthetic basalt was mixed with 15 wt. % B_2O_3 and the mixture melted at 1300° C. The fused mass was then powdered in mortar. The resulting powder was used to prepare pellets of different composition which were cold pressed and then sintered at 1000-1300° C. More thorough grinding of the fused synthetic basalt : B_2O_3 material leads to a decrease in the leach rates of Mg and Ca by factor of 1.5 to 2 while retaining a low Cr leach rate. As in all previous cases, increasing the sintering temperature from 1100° to 1300^0 C decreased the leach rates for pellets with high uranium chromite contents.

Compared with the leach rates for the uranium chromite: synthetic basalt system, the leach rates of Mg, Cr, Ca and Si decreased when B_2O_3 was introduced into system, particularly for compositions with 50-70 wt. % uranium chromite. For example, at 50 wt. % uranium chromite, the leach rate of Mg and Ca from pellets sintered at 1100° C decreased by a factor of 28 and 9 respectively, when the B_2O_3 was introduced.

Uranium chromite: basalt + B_2O_3 systems.
The leach rates for pellets prepared, from uranium chromite powder and a powder prepared from a fused mixture of basalt with B_2O_3 are given in table III. The basalt + B_2O_3 mixture was prepared by mixing powdered basalt with 15 wt. %. B_2O_3, and melting the mixture at 1300° C. The cooled melt was ground to a powder using one of the two methods described below and then

mixed with the uranium chromite in the stated proportions. Pellets were prepared by cold pressing and then sintering at different temperature.

The following describes the two methods of preparation of the basalt + B_2O_3 mixture powder from the cooled melt.

In the first method for prepearing the basalt + B_2O_3 powder, the cooled basalt + B_2O_3 melt was ground in a mortar and the fraction less than 0.2 mm was used to prepare the pellets, which were sintered at 1100^o C. The leach test results for these pellets are given in table III. For this system, the leach rates of Mg, Ca, Si and B increases as the uranium chromite content increases from 50 to 90 wt. %. The leach rate for Cr in all cases is $< 1\times10^{-8}$ g/(cm^2.day).

In the second method used to prepeare the basalt + B_2O_3 powder, the cooled basalt + B_2O_3 melt was first ground in a mortar. The fraction less then 0.2 mm was collected and then further ground in aball vibromill. The leaching rate of pellets obtained from the basalt + B_2O_3 additive are given in table III. For this pellets leach rates for the elements studied decreased appreciably for pellets sintered at 1100^o C to 1300^o C except for Cr, for which the leach rate decreased for sintering temperatures from – 1000^o C to 1100^o C. The element leach rates for pellets having uranium chromite content of 80% or 90 wt. % decreased several fold, when the sintering temperature increased from 1000^o C to 1300^o C. The leach rate of boron from a 90 wt. % uranium chromite system and Si from an 80 wt. % uranium chromite system decreased strongly in this sintering temperature range.

Comparing the data in tables I and III it should be noted that the introduction of B_2O_3 in the uranium chromite: basalt system by the method studied results in durable, compact pellets at low sintering temperatures and these pellets have high chemical stability with respect to leaching in water.

In addition, comparing the data in tables IV and III it may be seen that the leach rates are similar and very low for both systems at equal uranium chromite content in the range 50-90 wt. %.

CONCLUSIONS.

In summary, an increase in sintering temperature and introduction of B_2O_3 via a powdered cooled melt of a mixture of B_2O_3 with basalt or synthetic basalt decreases the leach rate of all studied elements for the uranium chromite: basalt or uranium chromite: synthetic basalt system studied. The leach rate of Cr was so small, that after 15 to 36 days the dissolved Cr concentration was lower than the sensitivity of the analytical method. We explain this results on the basis of the high chemical stability of pure uranium chromite and by the formation of a layer of basalt-like material around the uranium chromite particles by melting of the additive during sintering; the results are considered proof of our initial concept. As the pellet size quality, and leach time is increased, and more sensitive analytical methods (radiometry, electric conductivity, element total, etc.) are used, more accurate values of the leach rates of Cr and other elements may be obtained for this systems. During the next phase of this work we plan to obtain such improved leach rates.

The introduction of B_2O_3 allows production of more compact, durable pellets at lower sintering temperatures, than without B_2O_3. Pellets with 80 wt. % uranium chromite content appear to offer optimum characteristics. Increasing the uranium chromite content from 80% to 90 wt.%

increased the leach rate of all studied elements. Therefore we are planning to concentrate further studies in the most promising ranger of 70 to 90 wt. % uranium chromite. Further work will include studies of uranium niobate, REE compounds, and mixtures there of in the same range.

We also plan to include hot pressing for pelletization in the above planned studies; from initial investigation, that method seems promising for production of a higher quality product.