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Technology - Feed Materials

AEC RESEARCH AND DEVELOPMENT REPORT

TOPICAL REPORT

on

IDENTIFICATION OF SLAG CONSTITUENTS FROM URANIUM
METAL PRODUCTION BOMBS

by

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Report No. BMI-258

-3-

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Report No. BMI-258

-4-

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IDENTIFICATION OF SLAG CONSTITUENTS FROM URANIUM
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ABSTRACT

X-ray and microscopic examination of slags from uranium metal production bombs which gave good and bad yields in the plant at St. Louis have indicated the significance of uranium oxide formation. Apparently the oxide (UO_2) results from reaction of the UF_4 with liner material, particularly with moisture in the liner.

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION AND SUMMARY.	6
EXPERIMENTAL WORK	7
RESULTS	9
DISCUSSION OF RESULTS.	16
Production Bomb Slags	16
Experimental Bomb Slags	17
CONCLUSIONS	18

LIST OF TABLES

Table 1. Description of Samples and Results of X-Ray-Diffraction Examination of Slags From Production Bombs	10
Table 2. Description of Samples and Results of X-Ray-Diffraction Examination of Products in Experimental Bombs . . .	14
Table 3. Description of Various Areas in Slag and Relative Intensity of the Diffraction Patterns for the Phases Present.	15

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-6-

INTRODUCTION AND SUMMARY

The need for metallic uranium has increased considerably in recent years, and methods of production have been modified to increase the yield and decrease the cost. Mallinckrodt Chemical Works is producing uranium metal by reduction of UF_4 with magnesium. Their improvements in methods progressed to the point that by January, 1951, they were able to obtain an average yield of 96 per cent. However, even with this increased yield, production did not meet the requirements of the Atomic Energy Commission program. In order to increase production, a continuous method of producing UF_4 from UO_3 was developed. This method was put into operation in March of 1951. Unfortunately, the yield of metal decreased simultaneously. Attempts were made by Mallinckrodt to show that this decrease was due to the method of preparing UF_4 ; however, no definite correlation could be established.

X-ray and microscopical examination of the source materials was begun at Battelle in June, 1951. No significant differences between UF_4 prepared before or after March of 1951 were revealed. Hence, a study of the slag from good- and bad-yield bombs was initiated during August, 1951.

The technique used to produce uranium metal at St. Louis is as follows. The steel bomb is lined by tamping dead-burned dolomite around a mandrel. A mixture of uranium tetrafluoride and magnesium is then charged into the bomb with tamping, and the charge is covered with a layer of dead-burned dolomite. The bombs are fired by external heating. Once started, the reduction is exothermic, and the molten uranium metal collects at the bottom of the bomb. After cooling, the solidified metal is removed from the bomb and separated from the slag and liner.

In general, a bad-yield bomb is one from which less than 96 per cent of the U is recovered as massive metal well separated from the slag. The unrecovered metal remains in the slag either as oxide or in the metallic state. The slags from bombs of high yield retain the U in the metallic state while those of low yield retain a large portion of the lost U in the oxidized state. The major portion of the uranium-bearing phase (U or UO_2) in the slag is found in a region near the bottom of the slag. However, a center region of cinder-like slag was found to contain UO , which signifies a limited amount of available oxygen in this region. The size of these two regions correlated directly with the loss of U in the slag. The difference in the state of oxidation and location of the oxide phase suggests two sources of oxygen in the bomb: (1) air trapped in the bomb during packing or oxide in the UF_4 , and (2) oxygen from a source external to the slag, such as the

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liner. The first source would account for the existence of cinder-like pockets containing UO , protected against further oxidation by the surrounding slag layer. The second source might account for oxidation of the U after partial separation from the slag. This would require penetration of oxygen through the slag, a rather unlikely event. It is possible, however, that the U is reoxidized to UO_2 before separation. The UO_2 would then settle to the bottom if the slag remained molten for sufficient time. This alternative seems more likely. Since magnesium will reduce the oxides of uranium and since very little or no Mg spheres are present in bad-yield slag, it is possible that if a larger excess of Mg had been used some of the bomb yields would have been improved.

The loss of U as unseparated metal in the slag is influenced by the rate of settling of the U in molten slag. The melting point of the slag is determined by its composition. X-ray and microscopic studies have shown that the major portion of the slag is MgF_2 . Other phases identified were CaF_2 , MgO , UO_2 and UO . These phases vary in relative amounts and influence the macroscopic appearance and melting point at various regions of the slag. In order to have a low-melting slag, the higher melting compounds MgO , UO , and UO_2 must be kept at a minimum. On the other hand, CaF_2 lowers the melting point of MgF_2 from 1260°C . to as low as 950°C . at the eutectic composition of 45 mol. per cent CaF_2 . In the production bombs, the CaF_2 is derived from the CaO in the liner. The higher melting oxides either increase the melting point by solution in the slag or, by their presence as a solid suspension in the slag, increase its viscosity, thus diminishing the rate of separation of the U and slag.

A study of the reaction products from several test bombs which were heated to temperatures just below that required for firing shows that some reaction occurs in the bombs at the lower temperatures. The UF_4 adjacent to each Mg particle has been at least partially reduced. The completely reduced U was in most cases reoxidized. It was evident from this study of low-temperature reactions that UF_4 is reduced to UF_3 , then to metallic U, by the Mg. However, in the study of production-bomb slags, there was no evidence of partially reduced UF_4 .

Consideration of the possible sources of oxygen, and of the results of the present investigation, has suggested that moisture in the liner is a significant factor in reducing bomb yield.

EXPERIMENTAL WORK

The technique of producing uranium metal from the tetrafluoride by reaction with Mg in a steel bomb lined with dead-burned dolomite has progressed to the point that it is possible to reduce and recover as massive

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metal up to 97 per cent of the U added as the fluoride, in a single bomb. The average yield of metal from a 25-bomb run has been as high as 96 per cent. In March, 1951, the method of preparation of the UF_4 was changed from a batch to a continuous-flow method. At that time, the yield dropped off so that the average metal yield was lowered to 92 per cent. This loss amounted to approximately seven pounds of U per bomb. The slag in which the unrecovered U is trapped is difficult to reprocess. Because of a wide variation in bomb yield, regardless of the method of preparation of UF_4 , it was believed that a study of slags as well as the UF_4 would suggest a cause for the decrease in yield.

A cursory investigation was made of the UO_3 , UO_2 , and UF_4 , taken from periods of good and bad yield. No large differences were detected; however, the study has not been completed. The major effort was directed toward a study of slags from good- and bad-yield bombs.

Several slags broken out of production-bomb runs were submitted to Battelle for study. Although the samples received were only a portion of the complete slag, in some cases the pieces could be fitted together to form a complete horizon of the slag. The uranium yield corresponding to each of the slags was supplied by Mallinckrodt. In general, a yield is classified as "bad" if less than 95 per cent of the total U is recovered as sound metal. Factors initially believed to be the cause of low yield were (1) temperature of the slag during firing, and (2) changes in viscosity of the slag due to changes in composition. The temperature cycle of the bomb is recorded during firing. The bombs are heated in a furnace to approximately $650^\circ C.$, whereupon the exothermic reaction takes place, and a peak is observed in the temperature curve. The actual peak temperature reached varies considerably, depending upon the rate at which the charge reacts. In some cases, the reaction rate is very slow and no peak is observed. A bomb showing no peak in the temperature cycle is called a "dud" bomb. However, a peak in the temperature cycle is observed for most bombs. The appearance and composition of the slags indicate that temperatures of the order of $1500^\circ C.$ are attained.

In addition to the slags from the production bombs, several slags taken from experimental bombs were examined. The experimental bombs were not all fired, but some were heated to temperatures just below firing temperature and then cooled. These experiments were carried out to better understand how the reaction between Mg and UF_4 starts.

X-ray-diffraction methods use only a small amount of material. This required that a careful sampling of each slag would have to be made. Rather than to crush and mix comparatively large portions of slag to obtain average samples, thereby destroying the obvious inhomogeneity, spot samples were selected in such a way as to aid in explaining these inhomogeneities. The first selection of samples from each slag was made according to the

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macroscopic appearance (color and physical characteristics). A second selection was made on the basis of color and location in the bomb. The sampling for microscopic studies was made by cutting thin vertical sections which permitted observation of the distribution of the phases in the slag from top to bottom and from center to edge. The microscopic examination was undertaken as a supplement to the X-ray studies.

RESULTS

The X-ray methods, supplemented by some microscopic studies, have identified the compounds present in various regions of the several slags. It has been possible to estimate the relative amounts of the several compounds in these regions. The relative amounts of the compounds from sample to sample are estimated from the relative intensities of the strongest diffraction lines of each phase. However, no attempt was made to determine quantitatively the amounts present. The sample descriptions and results on the production-bomb slags are given in Table 1. Table 2 describes the samples taken from the experimental bombs and gives the corresponding phases identified. These experimental bombs were run at St. Louis to determine the reactions which take place between Mg and UF_4 at different temperatures during the firing cycle.

The slags obtained from the production bombs vary in composition from edge to center and from top to bottom. While the major phase in the slag is MgF_2 , as expected, the other phases, CaF_2 , MgO , and the uranium-bearing phases, vary considerably. At the liner-slag interface, CaF_2 and MgO are the major phases. The relative amount of CaF_2 decreases with increasing distance from the liner and the relative amount of MgO is a minimum in the region 1 to 2 inches from the liner. This suggests that CaF_2 is formed by erosion of the liner and diffuses into the slag and also suggests that the MgO has two sources, (1) the liner, and (2) oxidation of vaporized Mg. Microscopic study of the slag showed that the MgO adjacent to the liner has a larger particle size than the MgO found in the center of the slag. The increase in MgO content at the center of the slag suggests the presence of oxygen from an internal source, such as air trapped in packing the green salt and as UO_2 or UO_2F_2 included in the green salt. Further proof of the internal supply of oxygen is the finding of regions containing UO and high concentrations of MgO , surrounded by a shell-like solid slag. The variation in composition of the slag from top to bottom could not be completely investigated, owing to the absence of the top of several slag samples. The largest portion of the uranium-bearing phases is found at the bottom. In bombs which gave high yield, the U is found as metallic spheres in the bottom of the slag. In bombs which gave only moderately good yield, some U was lost as UO in the center of the slag as well as in the form of metallic

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TABLE 1. DESCRIPTION OF SAMPLES AND RESULTS OF X-RAY-DIFFRACTION EXAMINATION OF SLAGS FROM PRODUCTION BOMBS

Sample Nos. X-Ray Slag	Yield of Metal	Description of the Region Examined	Relative Intensity of Diffraction Patterns ⁽¹⁾									Remarks
			MgF ₂	CaF ₂	MgO	UO ₂	UO or UN	U	Mg	Ca(OH) ₂		
52B	273	97.6%	White, in gray marbled mass	VS	MF	VF	-	-	-	-	-	A solid slag containing large amounts of white dispersed in the gray, but only a small amount of regions 52C, 52D, and 52E; this slag has little or no U adhering to the bottom.
52C	"	"	Cinder-like region (small portion of the sample)	VS	MF	M	-	F	-	-	-	
52D	"	"	Gray, near bottom of slag	S	M	MF	-	VF	F	-	-	
52E	"	"	Metallic spheres in 52D (tarnished)	-	-	-	-	S	S	-	-	
52F	"	"	Dark-gray around metallic spheres at bottom	S	MF	S	-	F	F	-	-	
52G	"	"	Gray solid mass near center	S	M	MF	-	VVF?	-	-	-	
53B	276	97.3%	Liner powder adjacent to slag	-	F	VS	-	-	-	-	S	Same as Slag No. 52.
53C	"	"	Slag in first 1/2" from liner powder	S	S	MF	-	-	-	-	-	
53D	"	"	Gray slag 2" from liner	S	S	S	-	-	-	-	-	
53E	"	"	White slag 1" from liner (marbled region)	S	S	VF	-	-	-	-	-	
54B	803	96.0%	Silver metal sphere	-	-	-	-	-	-	VS	-	Same as Slag No. 52, but somewhat darker gray; chemical assay gave 0.96% U (54D).
54C	"	"	Gray slag adjacent to 54B	S	MS	MF	-	-	-	-	-	
54D	"	"	Gray slag 1" from liner (marbled region)	S	MS	M	-	-	-	-	-	
54E	"	"	White slag 1" from liner (marbled region)	S	S	F	-	-	-	-	-	
55B	926	89.0%	Dark-gray porous slag (bulk of slag)	S	S	MS	-	VF	-	-	-	A very dark-gray slag containing little or no white. A chemical assay gave 4.4% U content (55B).
55C	"	"	White to yellow, top of slag	MS	S	VF	-	-	-	-	-	
55D	"	"	Dark-gray-black, near to bottom	M	F	M	MS	-	-	-	-	
69A	25	Bad	Gray solid mass in center of slag	VS	VF	F	-	VF	-	-	-	The bulk of this slag was much the same as No. 52; however, a large section across the bottom (2" thick) was very brown and contained large amounts of metallic U.
69B	"	"	Gray cheese-like region 1/2"-2" from liner	VS	F	MF	-	VVF	-	-	-	
69C	"	"	Dark-gray cinder-like region in center	VS	VVF	MF	-	F	-	-	-	
69D	"	"	Dark-gray solid mass 2" from bottom	S	VF	M	VVF	VF	-	-	-	
69E	"	"	Dark-brown solid mass below 69D	MF	-	F	VS	-	-	-	-	

TABLE 1. (Continued)

Sample Nos.		Yield of Metal	Description of the Region Examined	Relative Intensity of Diffraction Patterns ⁽¹⁾								Remarks
X-Ray	Slag			MgF ₂	CaF ₂	MgO	UO ₂	UO or UN	U	Mg	Ca(OH) ₂	
70A	29	Good	Dark-gray cinder-like center	VS	MF	S	-	F	-	-	-	The sides and bottom of this slag had the appearance of Slag No. 52, but the center portion of 70A was large; this would indicate that the yield may be less than No. 52.
70B	"	"	Gray solid mass 1/2"-2" from liner (marbleized)	VS	M	MS	-	VVF	-	-	-	
70C	"	"	White drip on bottom of slag	M	VS	VF	-	-	-	-	-	
70D	"	"	Gray, from bottom of slag	S	F	S	F	?	MF	-	-	
67M	"	"	Dark-gray slag in first 1/2" from liner	F	S	S	-	-	-	-	-	
67O	"	"	White solid slag in marbleized region 70B	VS	M	F	-	-	-	-	-	
71A	35	Medium	Dark-gray cinder-like region in center	VS	VF	MS	-	MF	-	-	-	Same as Slag No. 54.
71B	"	"	Dark-gray in first 1/2" from liner (solid mass)	MF	S	S	-	-	-	-	-	
71C	"	"	Gray, adjacent to 71B and extending 1-1/2" into slag	VS	M	F	-	VVF?	-	-	-	
71D	"	"	Gray, adjacent to 71C and extending 2-1/2" into slag	VS	M	M	-	VF	-	-	-	
71E	"	"	Dark gray bottom slag	S	?	MS	MS	-	F	-	-	
82B	28	Bad	Black powder in cinder-like center	VS	F	MS	-	MF	-	-	-	A dark-gray slag with a large center region of cinder-like material as Sample 82B; the bottom has a layer of darker gray slag containing metallic U.
82C	"	"	Dark-gray solid slag in 82B	VS	M	MS	-	MF	-	-	-	
82D	"	"	White solid mass in marbleized region	MS	S	VF	-	-	-	-	-	
82E	"	"	Gray solid mass in marbleized region	VS	M	MS	-	VF	-	-	-	
82F	"	"	Dark-gray solid mass at bottom	VS	M	MS	-	VF	-	-	-	
82G	"	"	Dark-gray solid slag adjacent to liner	M	MS	M	-	VF	-	-	-	
83B	70	Bad	Black powder in cinder-like center	VS	M	M	-	MF	-	-	-	Same as Slag No. 82.
83C	"	"	Dark-gray solid slag in 83B	VS	M	M-	-	F	-	-	-	
83E	"	"	Gray solid mass around 83B	VS	M	MF	-	VVF	-	-	-	
83F	"	"	Dark-gray slag solid mass at bottom	S	S-	F	VF	-	-	-	-	
83G	"	"	Dark-gray slag adjacent to liner	S	S+	M	-	-	-	-	-	

TABLE 1. (Continued)

Sample Nos.		Yield of Metal	Description of the Region Examined	Relative Intensity of Diffraction Patterns ⁽¹⁾								Remarks
X-Ray	Slag			MgF ₂	CaF ₂	MgO	UO ₂	UO or UN	U	Mg	Ca(OH) ₂	
84B	71	Bad	Black powder in cinder-like center	VS	M	M+	-	F+	-	-	-	Same as Slag No. 82.
84C	"	"	Solid gray slag around 84B	VS	M	M	-	VF	-	-	-	
84D	"	"	Dark-gray slag adjacent to liner	VS	M+	M	-	-	-	-	-	
84E	"	"	Dark-gray slag near bottom	VS	F?	M+	MF	-	-	-	-	
85B	91	Good	Light-gray top of slag	S	S	M	-	-	-	-	-	A lighter gray slag than No. 82; however, the bottom is cleaner and has less metallic U; the center portion of a cinder-like region (85C) is larger.
85C	"	"	Black powder in cinder-like center	VS	M	MS	-	M-	-	-	-	
85D	"	"	Gray solid mass around 85C	VS	M	M	-	VF	-	-	-	
85E	"	"	Dark-gray, adjacent to liner	MS	S	S	-	-	-	-	-	
86B	92	Good	Black powder in cinder-like center	VS	M-	MS	-	MF	-	-	-	Same as Slag No. 85.
86C	"	"	Gray solid mass around 86B	VS	MS	MS	-	VVF	-	-	-	
86D	"	"	Gray solid mass in 86B	VS	M	M-	-	F	-	-	-	
86E	"	"	Dark-gray, adjacent to liner	VS	MS	M	-	VVF?	-	-	-	
87B	93	Good	Black powder in cinder-like center	VS	M	MS	-	M	-	-	-	Same as Slag No. 85.
87C	"	"	Gray solid mass around 87B	VS	M	M+	-	VF	-	-	-	
87D	"	"	Dark-gray adjacent to liner	VS	M	M+	-	?	-	-	-	
87E	"	"	Brown spots on bottom	M	-	VF	S	-	MF	-	-	
81B	Dud	Bad	Dark-gray solid mass 2" from bottom	S	-	S	MS	-	-	-	-	A dark-gray slag with pockets of white; each pocket has a brown to black ring between the white and gray slag.
81C	"	"	White slag in pockets of 81B	VS	-	-	F	-	-	-	-	
81D	"	"	Red-brown specks in 81B	M	-	VF	S	-	-	-	-	
81E	"	"	Brown to black ring interface between 81B and 81C	MS	-	M	S	-	-	-	-	
81F	"	"	Black sintered powder from top of slag	M	-	-	MS	-	S	**	-	
81G	"	"	Red-brown area in 81F	VVF?	-	VVF?	VS	-	MF	-	-	

TABLE 1. (Continued)

Sample Nos.		Yield of Metal	Description of the Region Examined	Relative Intensity of Diffraction Patterns ⁽¹⁾								Remarks
X-Ray	Slag			MgF ₂	CaF ₂	MgO	UO ₂	UO or UN	U	Mg	Ca(OH) ₂	
88B	-	Bad	Light-gray solid slag	VS	M	VF	-	-	-	-	-	} Same as Slag No. 69.
88C	-	"	Dark-gray to brown, just below 88B	M	-	VF	S	-	-	-	-	
88D	-	"	Filing from tranished metal spheres	F	-	-	MF	-	S	-	-	
88E	-	"	Red-brown spots in brown bottom	VF	-	-	VS	-	-	-	M-UN ₂	
88F	-	"	Brown bottom layer of slag	M	-	-	VS	-	M	-	-	
88G	-	"	White deposit on bottom of brown slag	VS	-	M	MF	-	-	-	VF-UN ₂	

S = Strong

VS = Very strong

M = Moderate

F = Faint

VF = Very faint

** = Removed

TABLE 2. DESCRIPTION OF SAMPLES AND RESULTS OF X-RAY-DIFFRACTION EXAMINATION OF PRODUCTS IN EXPERIMENTAL BOMBS

Sample Nos.		Description of Bomb and Portion Examined	Compounds and Relative Intensities of Compounds Identified	Remarks
X-Ray	Run			
74	-	UF ₄ + Mg fired in carbon bomb (no liner or insulation)		
74A	-	Brown slag from center of 74	VS - MgF ₂ + F - UO ₂	Apparently air entered the bomb oxidizing the U to UO ₂ .
74B	-	Dark-brown slag from bottom of 74	S - MgF ₂ + M - UO ₂	
75	-	UF ₄ + Mg fired in carbon bomb (insulated outside of bomb)		
75A	-	Light-gray slag adhering to bomb wall	VS - MgF ₂ + VF - MgO	This bomb gave a very high yield indicating the insulation aided in sealing the bomb.
75B	-	Gray slag at interface between slag and bomb	S - MgF ₂ + F UO ₂ + F - UN ₂	
76	5	UF ₄ + Mg heated in carbon bomb to 600° C., cooled		
76B	-	Black powder around each Mg particle	S - UO ₂ + M - UN ₂	
76C	-	Green powder around black powder of 76B	UF ₄	
77	-	UO ₂ F ₂ + Mg sandwiched between layers of UF ₄ + Mg heated in carbon bomb to 560° C.		
77B	-	Yellow powder from UO ₂ F ₂ layer of 77	S - UO ₂ F ₂	
77F	-	Black on Mg particle in UO ₂ F ₂ layer of 77	S - U ₃ O ₈	
77E	-	White on Mg particle in UF ₄ layer of 77	S - UF ₃ + F - MgF ₂ ?	
77G	-	Yellow-brown layer on Mg particle in UF ₄ layer of 77	S - MgF ₂ + F - UO ₂ + F - UN ₂	
91	-	UF ₄ + Mg heated slowly to 1000° C. in Fe bomb		
91B	-	Red-brown layer in resulting powder	S - UO ₂ + MS - U + F - MgF ₂	
91C	-	Gray-black powder	VS - U + M - MgF ₂ + VVF - UO ₂	
92	-	UF ₄ + Mg heated to 800° C. in open crucible		
92B	-	Black on Mg particle	U ₃ O ₈	
92C	-	Brown on Mg particle	UO ₂ + UF ₄	
93A	-	Mg vapor reacted with UF ₄ at 560° C. in vacuum	S - UF ₃ + F - UO ₂	

spheres near the bottom. However, in the case of very low yields, the major portion of the U is trapped in the bottom of the slag as U metal mixed with large amounts of UO_2 . Of the other components in the slag, it was observed that the relative amount of CaF_2 decreased from top to bottom. The relative amount of MgO was higher in the center of the slag than it was at the top or bottom.

The macroscopic appearance of the slag is influenced by composition. Table 3 shows the change in color, physical characteristics, approximate location, and relative intensities of the diffraction pattern for the various phases found in macroscopically different samples. The regions having the same appearance were found at approximately the same location in the several slags. The variation in size of the various regions appears to correlate with the amount of U metal recovered. However, these macroscopic differences have not been explained on the basis of the relative bomb yield. There are, however, two macroscopic observations that appear to correlate with bomb yield. Slags taken from bad-yield bombs have few or no Mg metal spheres trapped in the slag while many Mg metal spheres were observed in slag from good-yield bombs. It was also observed that slags from bad-yield bombs were lighter in color than the slag from good-yield bombs. This indicates a higher CaF_2 and lower MgO content in the slag from bad-yield bombs. This latter observation is confirmed by the X-ray studies except for the "dud" bombs.

TABLE 3. DESCRIPTION OF VARIOUS AREAS IN SLAG AND RELATIVE INTENSITY OF THE DIFFRACTION PATTERNS FOR THE PHASES PRESENT

Area No.	Color	Location in Slag	Massive Appearance	Relative Intensity of Diffraction Pattern						
				MgF ₂	CaF ₂	MgO	UO ₂	UO	U	Mg
1	Straw	Bottom	Metal spheres	-	-	-	-	-	S	-
2	White	Dispersed	Ditto	-	-	-	-	-	-	VS
3	Brown	Bottom	Solid	MF	-	F	VS	-	-	-
4	Gray black	Bottom	Solid	VS	-	S	M	-	?	-
5	Dark gray	Near bottom	Solid	VS	F	S	-	-	-	-
6	Medium gray	Side	Solid cheeselike	VS	M	M	-	-	-	-
7	Light gray	Top	Solid	VS	S	MF	-	-	-	-
8	White	Solid shell	Solid	S	S	-	-	-	-	-
9	Dark gray	Center	Powder	S	MF	MS	-	-	-	-
10	Black	Center	Powder	S	F	MS	-	MF	-	-
11	Gray	Edge	Solid	MF	S	S	-	-	-	-

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DISCUSSION OF RESULTS

Production Bomb Slags

The fifteen slags examined are believed to be a representative sampling of the various types of slags obtained under Plant 7 conditions. These slags were taken from bombs having a range in metal yield from 97 per cent to 89 per cent of the total uranium. Good or bad slags refer to the uranium metal yields, respectively, above or below 95 per cent of the total uranium in the bomb. The description of the bulk slag appearance is given in Table 1 along with the results and description of X-ray sampling. The results show that uranium is retained in the slag in two different regions, (1) the center, and (2) the bottom. In the center region, the uranium is found as UO . This phase is difficult to differentiate from UN owing to the similarity in the structure, the small difference in lattice spacing, and the other phases present in the sample. However, we believe this phase to be UO because of its location in the bomb. At the bottom of the slag, uranium is retained as metallic spheres and as UO_2 . Good-yield slags retain the uranium as metallic spheres with little UO_2 , while those of bad yield often have a large layer of UO_2 . Location, appearance, and composition of these two regions, (1) and (2), indicate that the reasons for loss of metal may differ. However, it is apparent that large losses of metal occur by oxidation as well as by trapping of U metal.

The source of oxygen in the bomb which is most significant in reducing the yield is not known. There are, however, several sources which may contribute: (1) air trapped in the bomb during packing, (2) oxygen included in the UF_4 as UO_2 and UO_2F_2 , (3) reaction of UF_4 with CaO to produce UO_2 and CaF_2 (this reaction alone does not deplete the charge of Mg, therefore, the reaction is an important source of UO_2 only if this compound is not subsequently reduced by Mg), (4) oxygen released as water from Ca(OH)_2 in the liner, and (5) air allowed to enter through a leak in the bomb. The first two and the last of these sources of oxygen are believed to be of limited importance owing to the high density of the packed UF_4 -Mg blend, the purity of the UF_4 , and method of sealing the bomb. However, it is obvious from the increased amount of CaF_2 in the bad-yield slag that the third or fourth source can furnish a large amount of oxygen. By a close inspection of the various slag samples, it was noted that the low-yield slags had very little or no Mg metal retained, while in the high-yield slags many Mg spheres were observed throughout. This would suggest that the yields from some slags might have been increased if an excess of Mg had been added. At least, the amount of U in the oxidized state would have been decreased.

The separation of metallic U from the slag requires that the slag remain liquid for sufficient time to allow the heavier U to settle to the

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bottom. The melting point of MgF_2 is 1260°C . The effect of CaF_2 , MgO , and UO on this melting point has been considered. CaF_2 and MgF_2 form a eutectic at 45 mol. per cent CaF_2 which melts at 950°C . The reduced melting point is, of course, desirable. The CaF_2 is obtained by reaction of the liner with MgF_2 , and possibly also with the UF_4 . Microscopic examination confirmed the existence of eutectic regions. Spot X-ray analysis of these regions showed this eutectic to be $\text{MgF}_2\text{-CaF}_2$. The effect of MgO , UO , or UO_2 upon the melting point of the slag is unknown. Since Mg will reduce the oxides of U and since excess Mg is added to the bomb, the effect of MgO on the melting point of the slag was considered first. Two sources of MgO are known, (1) the liner and (2) oxidation of vaporized Mg . Microscopic examination has shown that the MgO crystals near the liner are of large irregular shape while those found inside the slag are small cubes with rounded corners. Although the solubility of MgO in fused MgF_2 appears to be low, the rounded corners of the MgO cubes indicate some solubility in the slag at the temperatures attained. This could raise the melting point of the slag. The region in the slag (the center cinder-like region) which appeared as though it was never fully molten was higher in MgO content. However, the temperature gradient in the slag is unknown and the center may not have been at so high a temperature as other regions. It is interesting to note that the cinder-like center region also contains UO . If the MgO does not dissolve in the slag, it is quite possible that these solid particles suspended in the melt of CaF_2 and MgF_2 would affect the settling rate of the U particles.

Experimental Bomb Slags

Five slags from experimental bombs, Samples 74, 75, 76, 91, and 92 of Table 2, were heated to the approximate firing temperature. The results are given in Table 2. In Sample 74, a large amount of U was retained in the slag as UO_2 , while in Sample 75 very little UO_2 was detected. The latter slag appeared to have volatilized to the wall of the bomb, indicating a high temperature during firing. Spheres of Mg were found on the bottom of the slag adhering to the top of the bomb. The presence of these Mg spheres indicates a low oxygen content in the bomb, and in this case, the yield was high. These observations are in agreement with the concept of the adverse effect of oxygen on the yield of U metal.

The slag examined from Sample 91 was apparently taken from the region at the bottom of the slag. The U in this sample had not separated from the slag and remained as a powder rather than as a metallic mass. The temperature of the reaction was never high enough to melt the U . A large portion of the sample contained finely divided U powder mixed with MgF_2 . Thin layers of UO_2 were observed as a red-brown powder. Since Sample 91 was slowly heated to 1000°C ., the reaction of the Mg with the

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UF₄ progressed at a sufficiently slow rate to hold the temperature of the mass below the melting point of U. This would suggest that U might be lost in a production bomb as metal powder dispersed throughout the MgF₂ if a very slow rate of heating were employed. Owing to the insulating properties of the liner and of the UF₄, the center of the slag in production bombs may in some cases be subjected to such a slow heat treatment. This may account for the unmelted appearance of the slag at the center of some of the production bombs. In Samples 76 and 92 of Table 2, the presence of Mg and UF₄ shows that the reaction was incomplete. No U metal was found in these two samples. However, the presence of UO₂, UN₂, and U₃O₈ suggests that large amounts of air were available to reoxidize any uranium which had been reduced. It is questionable whether UF₄ heated in air to these temperatures would oxidize as completely as in this experiment.

Two samples, 77 and 93, had been heat treated at a temperature (560°C.) below that used to fire production bombs. Since a study of the effect of UO₂F₂ content upon bomb yield had shown that bombs containing 2 to 5 per cent of this phase gave better yields, it was decided to study the reaction of Mg with UO₂F₂. The Mg particles were mixed with UO₂F₂, and a layer of this mixture was sandwiched between layers of the normal blend of Mg and UF₄. This bomb was heated to 560°C. and cooled. The Mg particles in the UO₂F₂ layer became coated with a layer of black U₃O₈. In the normal blend layers, the Mg particles turned white. The white coating has been identified as UF₃ plus MgF₂. Since these samples were taken from the same run, the oxygen which produced the U₃O₈ must have come from the UO₂F₂. The finding of UF₃ by partial reduction at this temperature suggests the possibility of stepwise reduction in production bombs. Sample 93 was the product obtained by exposure of UF₄ to Mg vapor in partial vacuum at 560°C. Although no U metal was detected, considerable UO₂ was observed, far in excess of that present as impurity in the UF₄. Therefore, the UO₂ must have resulted from reoxidation of U. The presence of both UF₃ and UO₂ (reoxidized U) confirm the proposed stepwise reduction mechanism.

These low-temperature experiments indicate that Mg will begin to reduce the UF₄ at temperatures below that necessary for firing a production bomb. If in a production bomb, the heating rate is so slow as to permit the premature reaction to progress, the subsequent explosive reaction would be of lesser magnitude and the final temperature lowered.

CONCLUSIONS

The results of X-ray and microscopical examination of the slags represent scattered information, mainly of a qualitative nature, as to the

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phases present in very heterogeneous samples. The number of examples of slags from good and bad runs is insufficient to enable one to draw definite conclusions. The variation from slag to slag in any one class is large, and the distinctions between classes are, in many respects, not sharp. Nevertheless, an attempt will be made to summarize some of the most definite observations which appear significant in suggesting the reason for the variation of U yield.

- (1) The low yield is associated with the presence of extraneous oxygen in the bomb. When the yield is high, the residual U is found in the slag as metallic spheres, together with excess Mg. When the yield is low, the residual U in the slag occurs largely as oxide at the bottom of the slag, and very little free Mg is observed.
- (2) The amount of trapped air in the charge is too small to account for the low yield. Approximately the same amount is present in runs of high yield.
- (3) Likewise, the oxygen content of the UF_4 in the charge cannot vary enough in any one batch to explain the scatter in bomb yield from that batch. Although the oxygen content varies from batch to batch, the amount present is probably never enough alone to account for the amounts of UO_2 found in bad runs.
- (4) It seems unlikely that air sucked into a poorly sealed bomb could account for these results. If air leakage were the cause, the most likely time for this to occur would be on cooling, at which time the internal pressure might be below atmospheric. However, the reduced metal should be protected by the molten or frozen slag. The porosity of the slag does not appear to affect its protective action. Porous slags were observed when the yield was high, and massive slags when the yield was low, although the reverse was also noted.
- (5) The dolomitic lime liner has been suggested as a possible source of oxidation. If the liner is anhydrous, however, and HF is not present in the charge, the liner is not a source of extraneous oxygen. This would not explain the concurrence of low Mg and high UO_2 in low-yield runs. For example, one might argue that the UO_2 is formed by reaction of UF_4 with CaO in the liner. If, then, the UO_2 is reduced by Mg, the

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final reaction products differ only in that CaF_2 replaces some of the MgF_2 , and the yield should be high. If the UO_2 is not reduced, there should be more residual Mg in slags with large amount of UO_2 than when the UO_2 is low. This is not the case, however. The presence of moisture in the lime, however, would be very effective in lowering the yield, either by directly using up the Mg or by re-oxidizing the U.

- (6) The higher concentration of CaF_2 in the low-yield slags confirms the hypothesis of increased reaction with the liner, due to increased hydration in these cases. The viscosity of the fluid slag is sufficiently low to permit settling of the U-bearing phases. Since, however, CaF_2 lowers the melting point of the slag, the fluidity of the low-yield slag cannot be taken as an indication that the slag temperature attained in a bad run is as high as that reached in a good run.

Because of obvious loopholes in this argument, and missing information, the above statements can only be considered as a presentation of a working hypothesis. Means have been considered for reducing the possible effect of moisture on the reaction yield. These means include modifications of the liner, and insertion of a physical barrier.

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