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Chemical Technology Division

REACTION OF URANIUM OXIDES WITH CHLORINE AND CARBON OR CARBON MONOXIDE TO PREPARE URANIUM CHLORIDES

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ABSTRACT

The preferred preparation concept of uranium metal for feed to an AVLIS uranium enrichment process requires preparation of uranium tetrachloride (UCl_4) by reacting uranium oxides (UO_2/UO_3) and chlorine (Cl_2) in a molten chloride salt medium. UO_2 is a very stable metal oxide; thus, the chemical conversion requires both a chlorinating agent and a reducing agent that gives an oxide product which is much more stable than the corresponding chloride. Experimental studies in a quartz reactor of 4-cm ID have demonstrated the practicality of some chemical flow sheets.

Experimentation has illustrated a sequence of results concerning the chemical flow sheets. Tests with a graphite block at 850°C demonstrated rapid reactions of Cl_2 and evolution of carbon dioxide (CO_2) as a product. Use of carbon monoxide (CO) as the reducing agent also gave rapid reactions of Cl_2 and formation of CO_2 at lower temperatures, but the reduction reactions were slower than the chlorinations. Carbon powder in the molten salt melt gave higher rates of reduction and better steady state utilization of Cl_2. Addition of UO_2 feed while chlorination was in progress greatly improved the operation by avoiding the plugging effects from high UO_2 concentrations and the poor Cl_2 utilizations from low UO_2 concentrations. An UO_3 feed gave undesirable effects while a feed of UO_2-C spheres was excellent. The UO_2-C spheres also gave good rates of reaction as a fixed bed without any molten chloride salt. Results with a larger reactor and a bottom condenser for volatilized uranium show collection of condensed uranium chlorides as a loose powder and chlorine utilizations of 95-98% at high feed rates.

1. INTRODUCTION

The feed for an Atomic Vapor Laser Isotope Separation (AVLIS) process for uranium will be uranium metal.[1] The principal production of uranium metal for nuclear fuel cycles has previously been by batch metallothermic reductions of uranium fluoride (UF_4) using magnesium or calcium metal. If this batch metal production were used for a large AVLIS enrichment plant ($\geq 10^4$ ton U/year), the costs of the hydrogen fluoride (HF) feed, the calcium or magnesium feed and the disposal of magnesium fluoride (MgF_2) or calcium fluoride (CaF_2) wastes would be major parts of the total uranium enrichment costs. Alternate processes for preparation of uranium metal from UCl_4 allow recycling of Cl_2 from electrolytic cells.[2] The products of uranium ore refineries are uranium oxides—most commonly UO_3. The objective of this AVLIS development program was to determine practical process conditions for efficient production of UCl_4 from uranium oxides.

There is extensive background literature on the production of UCl_4 based on reaction of carbon tetrachloride with uranium oxides.[3] Such a process was used at Oak Ridge for producing calutron feed material. Despite this previous experience, a process based on the use of CCl_4 would not be desirable for the proposed continuous metallothermic reduction process in which chlorine values are recycled because of both the risks associated with CCl_4 and the fact that recycle of chlorine values would require process equipment for CCl_4 synthesis. Such difficulties could be avoided with a process involving direct reaction of chlorine, carbon and/or carbon monoxide, and uranium oxides.

A search of the technical literature did not reveal any report of the preparation of pure UCl_4 from uranium oxides, Cl_2, and C or CO. Canning demonstrated nearly complete utilization of Cl_2 for up to 90% chlorination of impure uranium oxides,[4] as a first step of an overall process for producing purified metal. He sparged Cl_2 through a graphite diffuser into molten KCl-NaCl to which he fed the impure oxides. After chlorination, the molten salt mixture was treated with magnesium metal for reducing uranium compounds and electro-refined to improve the metal purity. Lyon reported rapid reaction of uranium oxides with chlorine in molten NaCl-KCl at 850°C to produce UO_2Cl_2.[5] Gens studied the volatilization of uranium chlorides from nuclear fuels and also found the formation of some nonvolatile UO_2Cl_2.[6] Gibson reported complete chlorination of UO_2 using a block of carbon and Cl_2 in KCl-NaCl at 860°C as a first step in a process for producing purified UO_2.[7] These results, along with those using CCl_4 rather than Cl_2, report chlorination of uranium oxides and removal of oxygen as CO or CO_2.

The use of published thermochemical data for uranium oxide, oxychloride, and chloride compounds is a first step for identifying probable reactions for the desired chemical conversion. However, there are several reasons for uncertainties for such predictions. Uranium chemistry is complex with stable valence states of 3, 4, 5, and 6. Oxides, one or more oxychlorides, and chlorides have been identified at most of these valence states. The volatility of the chloride compounds increases with valence state while chemical stability decreases. All of the compounds have large negative heats and free energies of formation; hence, calculation of free energies of reaction generally involves the inherent uncertainties of small difference of large numbers. A detailed compilation of available thermochemical data for the various uranium oxide, oxychloride, and chloride compounds is presented in the Appendix. Evaluation of this body of data leads to the following general findings:

- At a given valence state, the oxychlorides are more stable than the chlorides.
- At a given valence state, the oxides are more stable than the chlorides.
- All additions of chlorine to oxides or oxychlorides of lower valence [less than U(VI)] are favorable to give oxychlorides of higher valance.
- The oxychlorides can be formed both by direct reaction of chlorine and by reaction of an oxide with a chloride.
- Production of UCl_4 requires a reducing agent whose oxide product is much more stable than the chloride; that is, it does not react with uranium chlorides. Carbon and carbon monoxide meet this criteria. Hydrogen does not and the oxide (water) reacts with uranium chlorides to produce HCl.

Figure 1 presents a summary of the expected thermochemistry of the uranium oxide, oxychloride, and chloride compounds at various uranium valence states. The phase relationships between tetravalent uranium oxide and chloride are shown in Fig. 2.[8] The phase diagram shows that there are three stable compounds over the entire range of composition—UCl_4, $UOCl_2$, and UO_2. There is a eutectic reaction between UCl_4 and the intermediate compounds, $UOCl_2$(UCl_4 + 50 mol % UO_2). The melting point of pure UCl_4 is 590°C. A minimum melting point of 545°C occurs at the eutectic composition of UCl_4 + 6.9 mol % UO_2. A maximum solubility of about 13 mol % UO_2 in molten UCl_4 is reported at 810°C. At temperatures from 810 to 855°C UCl_4 vapor is in equilibrium with solid $UOCl_2$. $UOCl_2$ decomposes at 855°C. At higher temperatures, vapor and solid UO_2 are in equilibrium. The reasonably high solubility of UO_2 in molten UCl_4 over the temperature range of 545 to 810°C suggests a desirable precondition for achieving rapid rates of reaction between chlorine, carbon/carbon monoxide, and UO_2 dissolved in molten UCl_4.

The present investigations were carried out to characterize the production of UCl_4 by a direct carbochlorination of uranium oxides in a molten salt medium and to identify the optimum conditions for accomplishing the conversion in the most economic fashion. Variables that have been considered include the physical and chemical characteristics of the oxide feed material, the use of carbon versus carbon monoxide as a reductant, the physical characteristics of carbon reductants, the effects of feed rates, and the effect of temperature.

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VALUES IN PARENTHESES: MINUS FREE ENERGY OF REACTION, 900 K, kJ/equiv MULTIPLIER OUTSIDE PARENTHESES: EQUIVALENTS/REACTION,

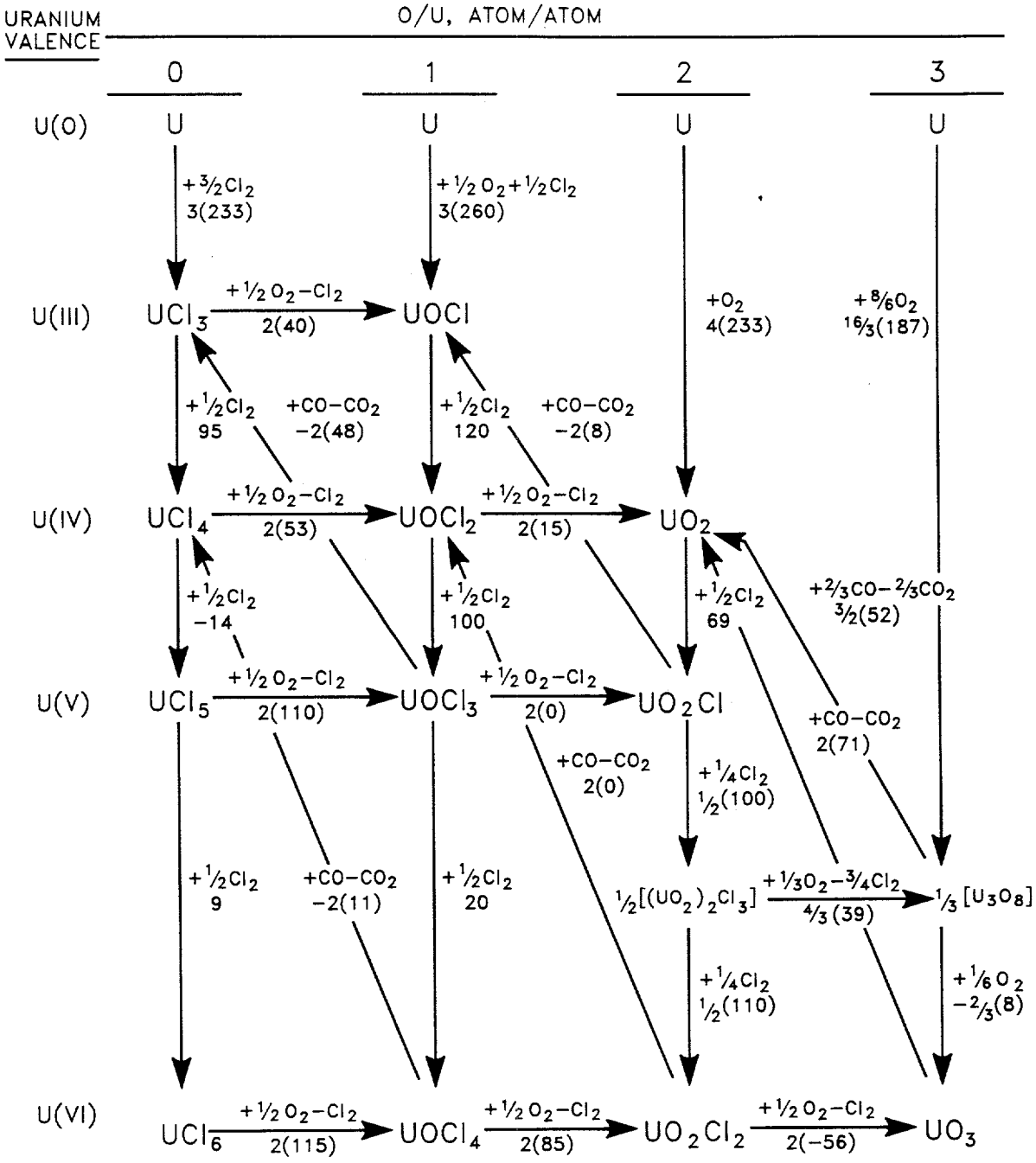

Fig. 1. Conversion reactions for U-O-Cl compounds.

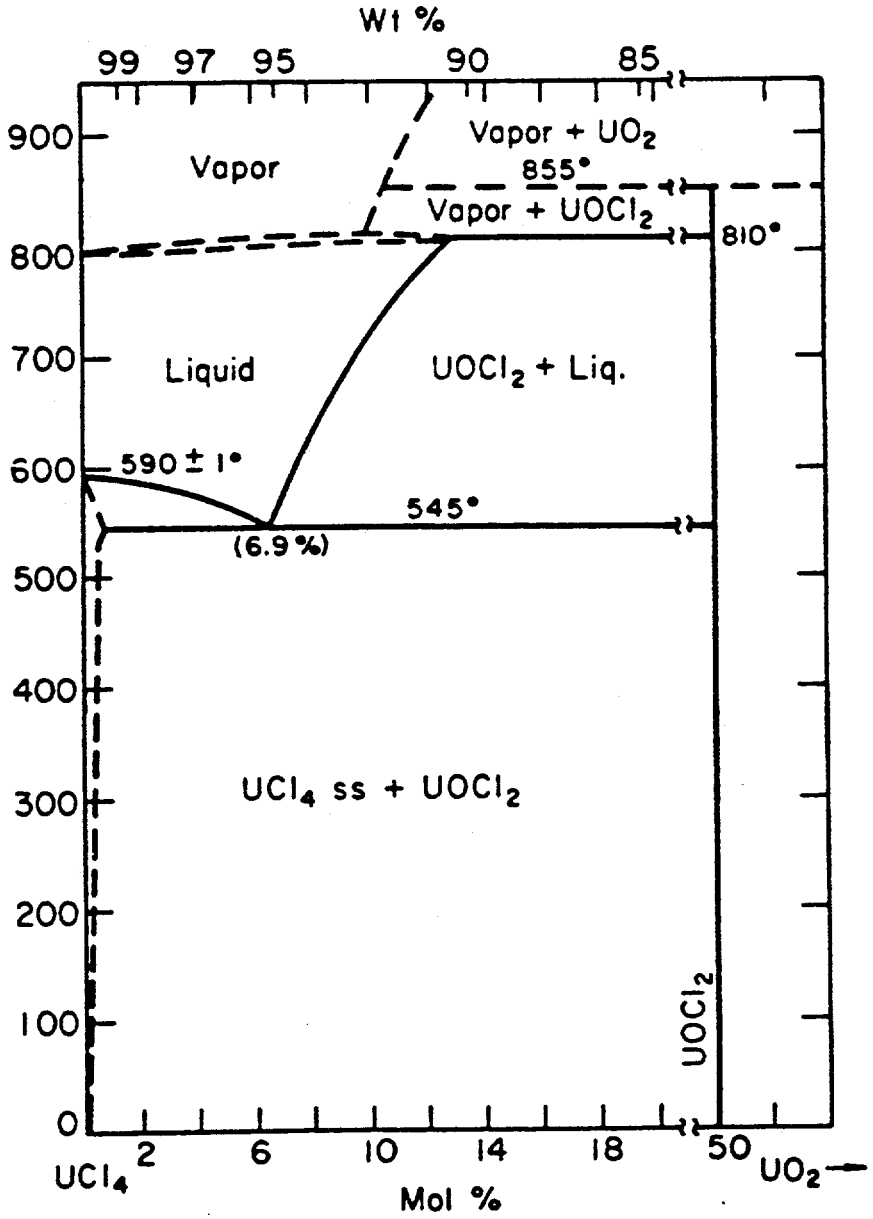

Fig. 2. Phase diagram for UCl_4-UO_2.[8]

2. EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental system was assembled from small flowmeters, 0.25-in. OD metal tubing and fittings, and quartz or borosilicate glass components fabricated by the Oak Ridge National Laboratory (ORNL) glass shop. For hot chlorine gas, the materials of construction were borosilicate glass for up to 450°C and quartz for the chlorination reactor up to 900°C. For chlorine gas at room temperature, Monel, Teflon, and Viton rubber were also used with some stainless steel for short time periods. Apparatus after the Cu-foil trap for Cl_2 was mainly stainless steel and plastic.

A diagram of the apparatus as used for Tests 5 to 18 is shown in Fig. 3 The initial arrangements as used for Tests 1 to 4 were described with the preliminary results.[3] The quartz reactor was 4-cm ID, 69-cm long, with a closed bottom and a 65/40 ball-joint socket at the top end (Fig. 4). The mating half of the ball joint had the fittings for all connections, including a gas sparger and the gas outlet. The initial charge was loaded into a quartz crucible of 3.2-cm ID, which was lowered on to a small pad of quartz wool on the reactor bottom. The initial reactor was fabricated with a quartz jacket for cooling from 38 to 53 cm above the bottom end. A simple borosilicate glass sleeve with "O" rings was used for air cooling after the initial unit. The gas sparger and the thermowell or UO_2 feed line were installed through the reactor cap using slip-fittings ("O" rings or Viton rubber sleeves) to allow length adjustments.

The apparatus and procedures allowed three different material balances for each test. The weight balances were probably the most accurate but gave only the overall run material balances. The weight measurements were:

1. The weight loss by a CuO reactor indicated the oxygen used to oxidize CO to CO_2.
2. The weight gain in a final Ascarite absorber showed the CO_2 that was produced from CO.
3. The weight gain for the first Ascarite absorber showed the CO_2 in the gas leaving the chlorination reactor.
4. The weight gain by the Cu-foil trap showed the Cl_2 in the gas leaving the chlorination reactor.
5. The weight gain by all reactor components equals the Cl_2 reacted plus the solids feed minus the C or O as CO, or CO_2 shown by a, b, and c. (Note that these quantities must allow for whether the oxidation reaction is C to CO_2, C to CO, or CO to CO_2.)

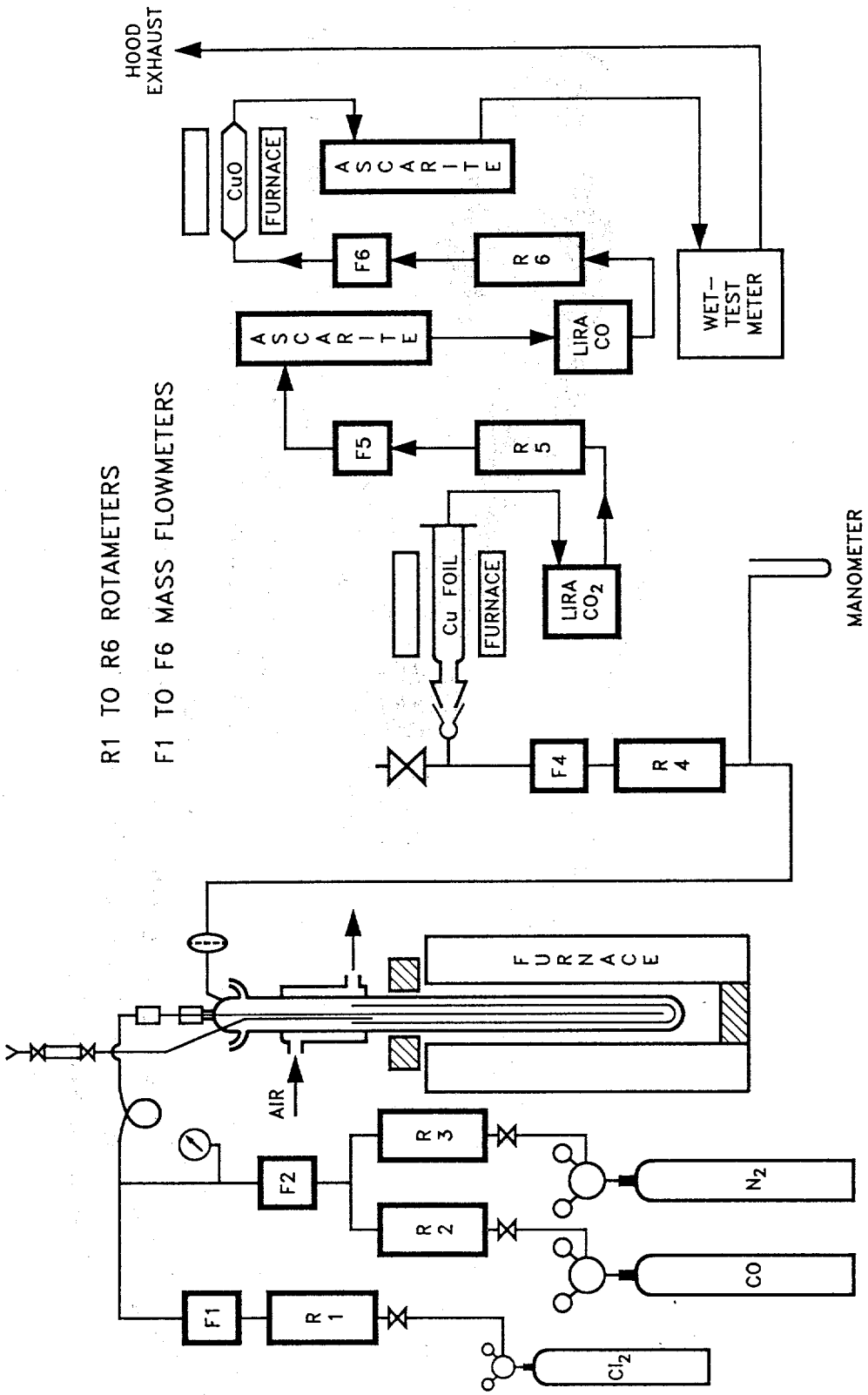

Fig. 3. Chlorination reactor (4-cm ID).

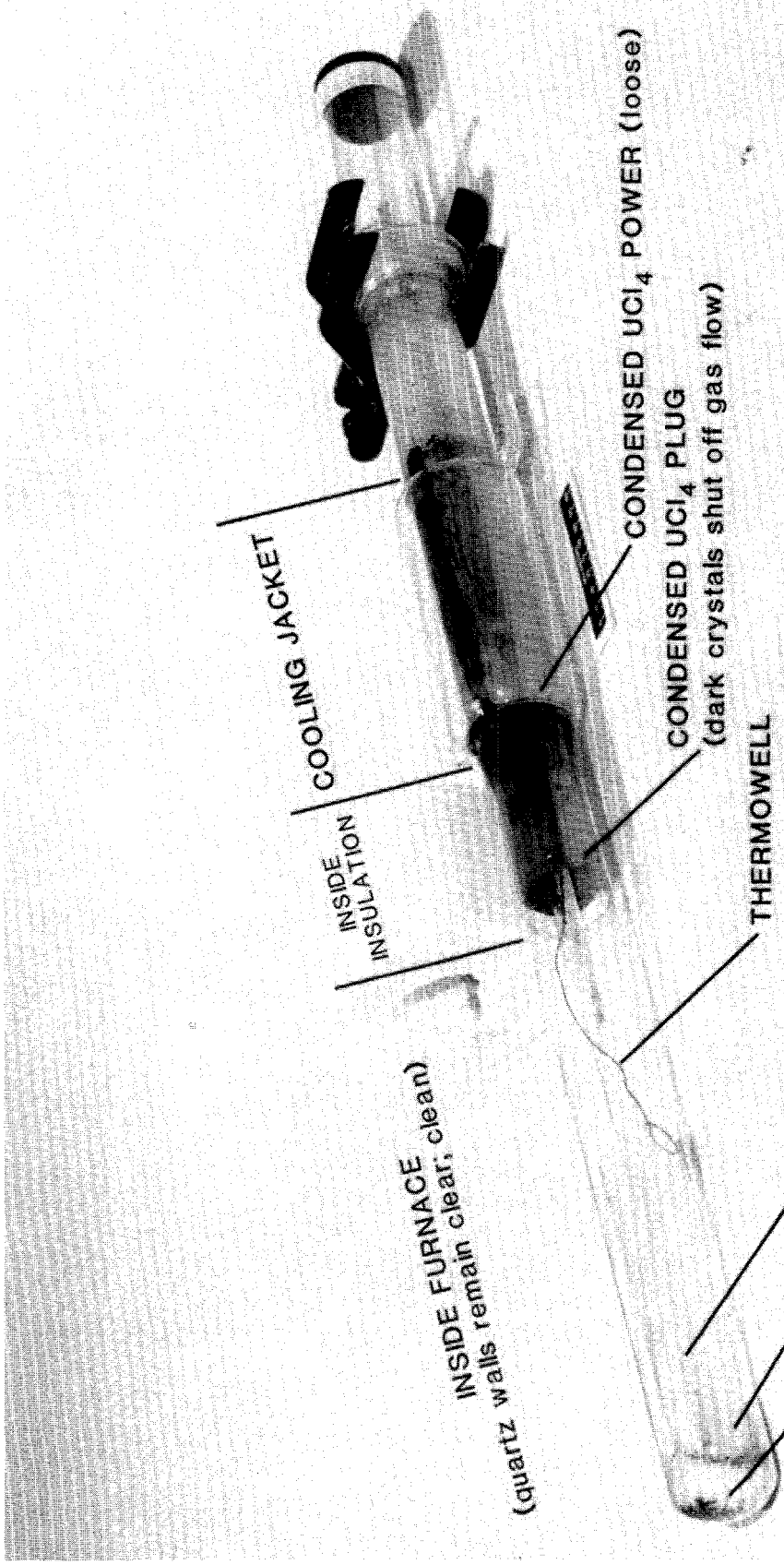

Fig. 4. Photograph of reactor as removed after MS-8.

The second material balances were from gas flow rates times concentrations. The concentrations and flows were:

1. 100% N_2 for diluent gas feed,
2. 100% N_2 for wet-test meter flow out,
3. 100% Cl_2 for Cl_2 feed,
4. 100% CO for CO feed,
5. in-line CO_2 measurement for gas out of the Cu-foil trap for Cl_2,
6. in-line CO measurement for gas out of the first Ascarite absorber, and
7. the N_2 content of the gas out of the first Ascarite is 1 minus CO.

The third, and generally least accurate material balances, are from differences in flow rates. These differences are:

1. reactor out minus Cu-foil trap out is the Cl_2 that leaves the chlorination reactor.
2. Cu-foil trap out minus the first Ascarite out shows the CO_2 absorbed.
3. the first Ascarite out minus the wet-test meter shows the CO oxidized to CO_2 and absorbed on the final Ascarite.
4. the Cl_2 feed, plus the N_2 feed, plus the CO feed, plus CO_2 or CO from C in the charge, minus the reactor out indicates the Cl_2 reacted with the charge.

The results found in the literature provide little information for selection between the chlorination process alternates. The reducing feed when using Cl_2 might be:

1. massive carbon or graphite blocks as reported,
2. carbon particles or powder,
3. carbon particles or powder mixed with uranium oxide powder and compacted, or
4. CO gas.

Any of the final three alternatives appear better than the massive blocks with respect to the reactivity, cost, and ease of replacement when consumed. Further, the reaction medium might be predominantly:

1. inert, low melting chloride salts,
2. uranium chlorides,
3. a fixed bed of uranium oxide-carbon granules or chunks, or
4. a fluidized bed of uranium oxide and carbon solids.

The phase diagram (Fig. 2) for UO_2-UCl_4 shows formation of $UOCl_2$ with all liquid for up to 7 mol % UO_2 at the melting point of UCl_4. This solubility of UO_2 in molten UCl_4 appears to be a desirable condition for easy and rapid chlorination and reduction reactions.

The chlorination condition of greatest interest for the AVLIS feed process was to react UO_2 and Cl_2 in a molten salt medium. Chlorination studies were planned for these conditions, and the selection of other conditions proceeded as follows:

1. The first tests were with a block of carbon for diffusers as favorably reported by Canning[4] and Gibson.[7]

2. After good reaction of Cl_2 and formation of CO_2 were demonstrated with the carbon diffusers, CO was tested as a more practical reducing agent.

3. After results with CO showed that the reduction reactions were much slower than the chlorination reactions, carbon powder was used to determine the effects of this reducing agent as compared to CO.

4. Since high UO_2 concentrations resulted in sparger plugging problems and low UO_2 concentrations gave poor utilizations of Cl_2, the experimental apparatus was modified to allow UO_2 feed while chlorination was in progress.

5. Tests were made with ball-milled UO_2 powder and with UO_2-carbon black spheres for comparison with the UO_2 spheres and the petroleum coke first tested.

6. Comparison tests were made with UO_3 spheres as feed and with a fixed-bed of UO_2-carbon black spheres without any molten salt.

7. The experimental apparatus was then modified to use a larger reactor with a bottom condenser.

The first four experimental tests were previously reported.[9] After eighteen tests (including the initial four) in a small apparatus, the equipment was modified to provide a larger reactor and a more useful condensation arrangement for product vapors.

3. RESULTS

Eighteen experimental tests were made in a quartz reactor of 4-cm ID and were directed toward the molten salt chlorination of uranium oxide. Three tests were not completed as planned because of failure of reactor components. One test was to check the procedures and material balances without chlorination. The remaining fourteen gave useful chlorination results. The test conditions are summarized as a tabulation (Table 1).

Table 1. Chlorination test parameters and conditions

MS test No.	Test dates	Furnace temperature (°C)	Reducing agent	Initial charge (mol)					Feed at temperatire (mol)			
				UCl_4	UO_2	C	$MgCl_2$	NaCl or LiCl	Cl_2	CO	UO_x	C
1	09-12-89	850	Graphite cylinder	0.016	0.06	2.4	0.46	0	0.16	0	0	0
2	10-05-89	700	Graphite cylinder	0	0.04	2.3	0.26	0.59	0.37	0	0	0
3	12-11-89 01-22-90	650 790	CO	0.08	0.11	0	0	0	a	a	0	0
4	03-21-90	625	CO	0.16	0.11	0	0	0	0.35	0.31	0	0
5	05-08-90	650	CO	0	0	0	0	0	0	0	0	0
6	05-10-90	650	CO	0	0	0	0	0	0.13	0.2	0	0
7	05-15-90	655	CO	0	0.12	0	0.54	0.53	0.56	0.6	0	0
8	06-04-90	645 680	CO	0.27	0.185	0	0	0	0.9	0.55	0	0
9	08-01-90	645	C*	0.29	0.146	0.67	0	0	0.43	0	0	0
10	08-13-90	645 680	C*	0.32	0.06	0.57	0	0	0.45	0	0	0
11A	08-20-90	635	None	0.24	0	0.67	0	0	0	0	0	0
11B	08-21-90	635	C*	0.24	0	0.67	0	0	0	0	0	0
11C	08-22-90	635 690	C*	0.24	0	0.67	0	0	0.35	0	0.056	0
12	09-04-90	635 680	C*	0.14	0.02	1.20	0.78	0.77	0.64	0	0.17	0
13	09-07-90	680	C*	0.29	0.02	1.2	0.78	0.77	0.70	0	0.185	0
14	09-25-90	710	C*	0.25	0.04	0.83	0.38	0.38	0.71	0	0.29	0
15	09-27-90	745	C*	0.56	0.02	0.83	0.38	0.38	0.78	0	0.24	0

Table 1. Chlorination test parameters and conditions (continued)

MS test No.	Test dates	Furnace temperature (°C)	Reducing agent	Initial charge (mol)					Feed at temperatire (mol)			
				UCl_4	UO_2	C	$MgCl_2$	NaCl or LiCl	Cl_2	CO	UO_x	C
16	10-16-90	705 675	C[c]	0.25	0.04	0	0.125	0.108	0.78	0	0.31	1.3
17	10-30-90	680	C[c]	0.58	0.02	0.9	0.125	0.108	0.35	0	0.11	0
18	11-06-90	700	C[c]	0	0.34	1.4	0	0	0.70	0	0	0
REACTOR SYSTEM CHANGED TO LARGER REACTOR, BOTTOM CONDENSER												
19	11-28-90	675	None	0	0	0	0	0	0	0	0	0
20	12-06-90	695	C[b]	1.47	0.15	4.5	0	0	0.66	0	0.06	0
21	12-18-90	677 699	C[b]	1.3	0.05	3.2	0	0	3.1	0	0.98	0
22	01-03-91	694 715	C[b]	1.7	0.25	4.7	0.21	0.21	2.5	0	0.71	0.35
23	01-16-91	731	C[d]	1.8	0.15	3.4	0.21	0.21	2.7	0	1.11	1.5
24	03-26-91	738 777	C[c]	0.96	0.15	2.00	0.3	0.3	2.87	0	1.11	1.17
25	04-03-91	777	C[c]	~1.2	0.15	2.00	0.3	0.3	1.97	0	0.65	0.25
26	04-24-91	774	C[c]	1.4	0.20	2.58	0.3	0.3	3.07	0	1.08	0
27	05-01-91	778	C[c]	1.8	0.30	1.1	0.3	0.3	0.66	0	0	0
28	05-14-91	778	C[c]	2.0	<0.1	3.1	0.3	0.3	4.46	0	1.93	0
29	05-29-91	778	C[c]	1.9	0.33	1.0	0.3	0.3	0.69	0.8	0	0
30	06-05-91	725	C[c]	2.0	0.15	2.7	0.3	0.3	2.81	0	1.07	0
31	06-11-91	690	C[c]	2.4	0.26	2.7	0.3	0.3	0.44	0	0	0

[a]Not measured.
[b]Petroleum coke.
[c]Carbon black.
[d]Petroleum coke in charge; carbon black in feed.

The progress of the chlorinations was indicated by the measurement of gas flow rates and concentrations during the tests. The overall or average results are shown by the material balances from reactor and trap weights after cool down to room temperature. Some results for the useful chlorination tests are tabulated (Table 2). Additional details by test numbers are in the Appendix. Each individual result can be interpreted in a number of ways since the overall process reactions result from a number of multiple step reactions.

Conclusions for important process parameters are discussed as separate sections. In general, a specific conclusion cannot be proven by one test result. Instead, the test results (Table 2 and the Appendix), along with thermochemical data, must be considered as a whole to justify the conclusions. Rapid reaction rates and removal of oxygen as CO or CO_2 were demonstrated in the first four experiments as previously reported.[9] The results of these initial tests are included in the tabulations, but the details in the initial report[9] are not repeated.

The test conditions (Table 1), and the brief tabulation of results (Table 2) do not clearly show how the process conditions, apparatus, and procedures were changed between experiments. Some of the most important changes in process conditions and the results are listed in Table 3. Important changes in apparatus and procedures, and the corresponding results are in Table 4. The material balances tabulated for chlorine (Table 5) and oxygen and carbon (Table 6) are averaged values with more weight to the more accurate mass measurements.

3.1 REACTIONS OF CHLORINE

All of the chlorination studies were done with uranium oxides and the reducing agent in the reactor at temperature when the chlorine flow was started. All tests show that the initial reactions of chlorine go very well without any significant concentration of chlorine in the exit gases. This was true when the initial charge contained melts of UCl_4, $MgCl_2$-NaCl or $MgCl_2$-LiCl, UCl_4-$MgCl_2$-NaCl, or a fixed bed of UO_2-C particles. The reaction rates for chlorine can be much higher than the rates of reduction indicated by CO or CO_2 flows. This result, thermochemical data, and some melt analyses indicate that the chlorine reacts by "oxidizing" U(IV) to higher valances; that is, the chlorine adds to the U(IV) compound to give U(VI) or perhaps U(V) compounds. Reaction of Cl_2 with UO_2 or oxychlorides is more favorable than reaction with UCl_4 to give UCl_5 or UCl_6. After U(IV) oxides or oxychlorides are depleted in concentration, UCl_4 is reacted to give UCl_6 or UCl_5 that are much more volatile.

Table 2. Chlorination test results

MS test No.	Furnace temp. (°C)	Overall/average run result[a] (%) Cl_2 feed reacted	Overall/average run result[a] (%) O_2 in UO_2 evolved	Cl_2 reacted / UO_2 feed atom Cl / mol UO_2	Principal conclusions and results
1	850	~50	ND[a]	~3.0	UO_2+Cl_2 + graphite → $CO_2+UCl_4+UO_xCl_y$.
2	700	~50	ND	small	Most of Cl_2 reacted with Monel sparge tube.
3	650	ND	ND	small	$UO_3+CO \rightarrow UO_2+CO_2$. Severe plugging of
	790	ND	ND	ND	sparger (perhaps $UOCl_2$). Nearly all of uranium volatilized out of crucible.
4	625	42	40	2.8	Consistent material balances, gas flow rates and gas concentrations. Condensed solids were predominantly UCl_4 while charge was half UCl_4 and half oxychlorides.
5	650	–	–	–	Quartz reactor broken.
6	650	0	–	0	Operator qualification completed.
7	655	38	<10	2.3	$UO_2+Cl_2+CO \rightarrow UO_2Cl_2+CO$ with little removal of O as CO_2. Apparently UCl_4 is necessary for reduction by CO.
8	645	30	55	2.8	The results of MS-4 were duplicated with good material balances. The rate of CO_2 evoluation showed little variation with temperature, Cl_2 rate, and sparger immersion. Complete plug by condensed solids.
	680				
9A	645	40	70	2.5	The C gave CO_2 without any detectable CO.
9B	645	0	0		Condensed solids plug of same appearance as MS-8. Leaks at the in-reactor sparger coupling resulted in low CL_2 utilizations.
10	645	36	>100	4.2	Condensed solids plug of same appearance as 680MS-8 and MS-9. Total material balalnce for MS-9 and MS-10 indicates complete conversion of UO_2 to UCl_4.
11A	635				No condensed UCl_4 without gas sparge.

Table 2. Chlorination test results
(continued)

MS test No.	Furnace temp. (°C)	Overall/average run result[a] (%) Cl_2 feed reacted	O_2 in UO_2 evolved	Cl_2 reacted / UO_2 feed atom Cl / mol UO_2	Principal conclusions and results
11B	635				Low UCl_4 volatility in agreement with UCl_4 vapor pressure without Cl_2.
11C	635 690	40	>80	~5.0	The feed of uranium oxide spheres into the UCl_4-C with Cl_2 gives an immediate evolution of CO_2 that peaks in a few minutes.
12	635 680	65	115	4.6	The rates of CO_2 evolution and the utilization of Cl_2 increased as the oxygen inventory was increased by successive additions of uranium oxides. A 50% increase in Cl_2 rate gave a 20% increase in CO_2. A 45°C higher temperature gave 60 to 80% increases in CO_2.
13	680	60	100	4.0	At 680°C, some point utilizations of Cl_2 were 100% and average values for 30 to 60 min were 80%.
14	710	92	102	4.0	Excellent Cl_2 utilization and conversion without excessive volatility of uranium.
15	745	63	106	3.9	Same type of plug as observed for 100% UCl_4 in MS-8, -9, -10, and -11.
16	705 675	92	115	4.2	Flow rates showed ≥99% utilization of Cl_2 until end of test when oxides were depleted. At 705°C, about 10% of the oxygen evolution was as CO. This decreased to a low value at 675°C. Carbon black is more reactive than coke.
17	680	65	145	3.8	UO_3 feed gives more complex reactions than UO_2. Uranium is more volatile with UO_3 feed. Cl_2 utilization is lower.
18	700	88	120	3.8	UO_2-carbon black gel spheres react well without molten salt. Typical dark plug of condensed solids stopped run while CO_2 rate was still high.
		Reactor System Changed To Larger Reactor; Bottom Condenser			
19	675				Mechanical and thermal performance of new components are good.

Table 2. Chlorination test results
(continued)

MS test No.	Furnace temp. (°C)	Overall/average run result[a] (%) Cl_2 feed reacted	O_2 in UO_2 evolved	Cl_2 reacted / UO_2 feed atom Cl / mol UO_2	Principal conclusions and results
20	695	85	117	4.9	About 0.17 mol condensed U collected as powder. Deposits on quartz wall above furnace and inside insulation below furnace.
21	677 699	94	107	5.0	0.77 mol condensed U collected as powder. Condensed U on vessel walls was about 0.59 mol or ~40% of volatilized U. Good operation except for two feed-line (UO_2) plugs.
22	694 715	82	120	4.4	Cl_2 utilization near 100% for 1 h. When Cl_2 utilization decreased, addition of 2 g C-black (48 g C-core in charge) doubled CO_2 evolution. N_2 purge eliminated UO_2 feed plugs. Different UO_2 feeds showed same reaction rate.
23	731	72	75	3.4	Quartz crucible cracked -- probably during heatup. A quartz baffle above crucible prevented UCl_4 deposits in top of reactor. Other results compromised by cracked crucible.
24	738 777	95	130	4.3	Reduction rate equaled chlorination rate. CO_2 rate = 0.5 Cl_2 rate = UO_2 feed rate; 141 g in product jar. Rates of reaction determined by Cl_2 feed rate without effects from temperature or the amounts of UO_2 or C inventory.
25	777	92	140	4.5	The MS-24 results confirmed with doubled UO_2 (0.60 mol/h) and Cl_2 (1.25 mol/h) feed rates. Condenser cross section plugged by dense solids.
26	774	92	120	4.4	The MS-24 and MS-25 results confirmed at higher UO_2 and Cl_2 feed rates; 329 g in product jar or 67 mol % of UO_2 feed.
27	778	95	160	4.2	Material specimens exposed for 6 h. Cl_2 utilization and percentage collection of product solids about same at the low rate and five times higher rate.
28	778	93	120	4.3	The MS-24 to MS-26 results confirmed at flow rates up to 2.8 mol/h Cl_2 feed. Continuous feed for UO_2 demonstrated, but plugs in feed line were troublesome. Reactor cross section plugged above condenser.

Table 2. Chlorination test results
(continued)

MS test No.	Furnace temp. (°C)	Overall/average run result[a] (%) Cl_2 feed reacted	Overall/average run result[a] (%) O_2 in UO_2 evolved	Cl_2 reacted UO_2 feed atom Cl mol UO_2	Principal conclusions and results
29	778	98	145	4.2	Material specimens exposed for 6 h with CO in the sparger gas. Cl_2 utilization and product collection results of MS-27 were confirmed. Thermowell in melt shows salt temperatures of about 730°C.
30	725	97	125	4.4	Good Cl_2 utilization at lower temperatures, salt temperatures of about 650°C. High N_2 flow to sparger gave high U vaporations at lower melt temperatures; 73% of condensed U in product jar.
31	690	97	110	3.4	Short period of Cl_2 flow did not complete conversation of UO_2. Cl_2 utilization good at melt temperature of 645°C. Dip samplers demonstrated removal of samples of melt.

[a]ND - not determined (measured).

Table 3. Changes in process conditions and results

Change	First test with change	Results from change
CO reductant in place of finned graphite cylinder	3	Evolution of CO_2 at lower temperatures.
UCl_4 as the only chloride salt (no $MgCl_2$-LiCl-NaCl)	3 8	Much higher rates of CO_2 evolution. Severe plugging of sparger at high UO_2/UCl_4 ratios.
$MgCl_2$-LiCl or $MgCl_2$-NaCl melt without UCl_4	2 only 7 only	No detectable CO_2 or CO, but good Cl_2 utilizations.
Petroleum coke particles in place of CO	9	Better (higher) Cl_2 utilizations, more complete removal of oxygen.
UCl_4 without gas sparge	11A only	No volatilization of U.
UCl_4 with N_2 sparge (No Cl_2)	11B only	Volatilization of U is small, in agreement with UCl_4 vapor pressure.
$MgCl_2$-NaCl eutectic as a diluent for UCl_4	12 to 17 22, 23	Much lower volatility of U, no crucible plugs at 685 or 710°C.
Feed of UO_2 during operation	12	Much better utilizations of Cl_2 (probably lower U volatility), but $MgCl_2$-NaCl addition at same time is larger effect.
Feed of UO_3, in place of UO_2	17 only	More complex reaction; several unwanted effects including lower Cl_2 utilization and higher U volatility.

Table 4. Changes in apparatus and procedures

Change	First test with change	Results from change
Cu foil trap for Cl_2 in place of thiosulfate scrubbers.	3	Good measurement of amount of Cl_2 trapped; better operation of Ascarite traps for CO_2.
In-line measurement of CO_2 and CO concentrations.	3	Real-time indications of the rates of reaction.
Monel sparger for Cl_2 feed.	2 only	Cl_2 reacted with Monel, then bypassed without reaction.
Open end to perforated sparger; perforated sparger to open end.	4 10	Not important to plugging; a 45° cut open end is best.
Shop calibrations of flow meters.	9	Much better accuracy for Cl_2, CO_2, CO rates from flow differences; better material balances from flow rates and concentrations. However, calibrations change with exposure to Cl_2.
Long crucible with top extending above insulation.	9	Allows easy removal of condensed solids or return to charge by melting.
Long quartz sparger without coupling in reactor.	10	Eliminated leaks and coupling failures as cause of low Cl_2 utilizations.
Feed of UO_2 particles during chlorination.	11C	Much better operation with respect to Cl_2 utilization, sparger plugging, and reduced volatility of U.
Larger reactor and bottom condenser.	19	60% of condensed U as powder on the bottom.

Table 5. Chlorination test material balances: chlorine

Test No.	Cl_2 product (mol)				Total Cl_2 (mol)			Cl_2 utilization (%)			Cl_2/UO_2 reacted
	Cu trap Wt[a]	Cu trap FD[b]	Reactor Wt	Reactor FD	Wt	FD	Feed FC[c]	Cu trap Wt and feed FC	Wt	FD	(mol/mol)
4	0.20	0.25	0.11	0.095	0.31	Not measured	0.35	43	35	Not measured	0.91
7	0.35	0.43	0.21	0.07	0.56	0.50	0.56	38	38	14	~1
8	0.60	0.59	0.26	0.20	0.86	0.79	1.06	43	30	19	1.4
9	0.25	0.14	0.15	0.09	0.40	0.46	0.43	34	38	39	1.0
10A	0.29	0.29	0.16	0.15	0.45	0.44	0.47	38	36	34	2.6
11C	0.21	0.18	0.17	0.12	0.38	0.30	0.33	36	45	40	2.7
12	0.23	0.18	0.40	0.49	0.63	0.67	0.64	64	63	73	2.4
13	0.31	0.27	0.38	0.45	0.69	0.71	0.71	56	55	63	2.0
14	0.062	0.04	0.65	0.74	0.71	0.78	0.71	91	91	95	2.2
15	0.30	0.20	0.50	0.53	0.80	0.77	0.72	58	63	73	2.2
16	0.062	0.048	0.74	0.73	0.80	0.78	0.76	92	92	94	2.1
17	0.111	0.18	0.24	0.18	0.35	0.36	0.36	69	68	50	1.6
18	0.096	0.07	0.65	0.53	0.75	0.60	0.70	86	87	88	1.8
20	0.09	0.13	2.82	0.55	3.08	0.68	0.66	86	92	81	2.7
21	0.17	0.38		2.30		2.68	2.68	94		86	2.4
22	0.44	0.37	1.98	2.31	2.42	2.68	2.39	82	82	86	2.2
23	0.75	0.75	1.6	2.07	2.3	2.82	2.68	72	67	73	1.7

[a]Wt indicates weight measurements.
[b]FD indicates differences in flow rates.
[c]FC indicates gas flow times concentration.

Table 6. Chlorination test material balances: carbon and oxygen

Test No.	CO feed by FC[a] (mol)	CO out of reactor (mol)				CO_2 out (mol)			Percent of UO_x oxygen out	CO_2 out/ Cl_2 reacted (mol/mol)
		From CuO Wt[b]	From abs. Wt[b]	From FC	From FD[c]	From abs. Wt[b]	From FC	From FD		
4	0.23	0.21	0.22	0.24	Not measured	0.086	0.077	0.084	40	0.8
7	0.89	0.67	0.64	0.73	0.56	0.05	0.01	~0	~10	<0.1
8	0.49	0.37	0.37	0.45	0.42	0.20	0.23	0.22	55	0.8
9	0	0	0	0	Not measured	0.10	0.09	0.07	70	0.6
10A	0	0	0	0	0	0.14	0.11	0.11	~200	0.9
11C	0	0	0	0	0	0.13	0.12	0.06	~200	0.8
12	0	0.01	0	0	Not measured	0.31	0.24	0.26	140	0.7
13	0	0	0	0	<0.01	0.21	0.15	0.16	100	0.53
14	0	0	0	0	Not measured	0.34	0.33	0.27	100	0.47
15	0	0.01	0	0	0	0.28	0.23	0.20	110	0.53
16	0	0.03	0.03	0.04	0.06	0.44	0.41	0.38	120	0.55
17	0	<0.01	0	0	<0.02	0.27	0.21	0.27	140	1.2
18	0	0.07	0.06	0.09	0.05	0.38	0.46	0.45	120	0.57
20	0	<0.01	0	0	0	0.24	0.24	0.27	114	0.42
21	0	<0.01	Not measured	0.02	0	1.03	0.88	1.03	100	0.41
22	0	0	0.02	0	0	1.09	1.15	1.21	120	0.55
23	0	0.02	0.02	0.05	0	0.95	0.97	0.81	75	0.48

[a]FC indicates gas flow times concentration.
[b]Wt indicates weight measurements.
[c]FD indicates differences in flow rates.

than UCl_4. This operating condition results in large losses of Cl_2 to the off-gas. Either the completeness of reaction of Cl_2 is limited by a less favorable equilibrium or the UCl_5 or UCl_6 decomposes as the vapors cool to give condensed UCl_4 and Cl_2. Operation with UO_3 as the feed instead of UO_2 also gave higher volatilities of uranium and larger losses of Cl_2. This result also indicates that U(IV) oxides or oxychlorides are very helpful to high utilizations of chlorine.

3.2 UTILIZATION OF CHLORINE

High utilization of chlorine required a good inventory of U(IV) oxides and oxychlorides in the reactor charge. The initially charged UO_2 supplied this inventory so that chlorine utilizations were always high when the chlorine feed was started. Continued high utilizations with complete chlorination required the reduction of U(VI) back to U(IV) at rates that prevented depletion of U(IV). Continued high utilizations were demonstrated using carbon as the reductant and reactor temperatures of $\geq 670°C$.

The minimum conditions to assure high chlorine utilizations for steady-state operation were not clearly determined. The following conditions gave poor chlorine utilizations of <70% (i.e., more than 30% of the feed chlorine was trapped from the exit gas (see Table 5).

1. All tests with CO as the reductant. (The best combination of higher temperatures and an optimum continuous feed of UO_2 might give higher chlorine utilization using CO.)
2. All tests with reactor temperatures near 630°C.
3. All operation with low concentrations of oxygen in the reactor charge. The limit on oxygen concentration depends on the Cl_2 feed rate and the concentration and reactivity of the carbon. Melts as low as 2 mol % oxides–98 mol % chloride can give good chlorine utilizations, but there is not enough information to determine limits. Because of this effect, operation at conditions intended to complete the conversion of UO_2 to UCl_4 gave higher chlorine losses to the off-gas.

When chlorine utilizations were good, the Cl_2 removed in the Cu trap was only a small percentage of the total gas flow. The calibrations of the two flow meters changed continually, and calculations of flow differences using separate calibrations of the two meters did not give useful measurements of the small Cl_2 losses. Finally, the whole run Cl_2 losses measured by the Cu trap weight gain were used to calculate meter factors that match the whole run flow differences to the Cu trap result. These meter factors gave much more consistent results for the short period Cl_2 losses. Some results from the large reactor tests using carbon black (all melt depths of 7 to 10 cm) show Cl_2 losses of 2 to 4% for a range of Cl_2 feed rates (Table 7).

Table 7. Chlorine losses versus Cl_2 feed rates using carbon black at ~730°C.

Test period	Cl_2 feed (cm^3/min)	Cl_2 losses (%)
27	43	2.6
24A	230	1.8
24B	230	4.3
25A	460	2.9
25B	460	3.3
26A	635	2.2
26B	770	4.3
28A	622	3.3
28B	838	4.0
28C	842	3.4
28D	1032	4.5
28E	1026	6.8

The higher losses near the end of test MS-28 may have resulted from an unintended depletion of the UO_2 inventory. After the UO_2 feed was ended, the appearance of high Cl_2 losses and the sharp decrease in CO_2 concentration indicated only 2 to 3 min (12 to 18 g of UO_2) before the inventory was grossly depleted.

These results show little variation in chlorine losses for a wide range of UO_2 and Cl_2 feed rates. Using carbon black at 730°C allowed high rates of reaction, but the Cl_2 losses remained $\geq 2\%$ at the most favorable conditions.

3.3 EFFECTS OF URANIUM OXIDE PROPERTIES

The feeds to an AVLIS plant will be uranium ore concentrates from refineries. Since a representative sample or a specification of typical properties was not available, the chlorination tests were made with several uranium oxides available at ORNL. Some measurements for these materials are in Table 8.

Results of chlorination tests indicated that the chlorination reactions are simpler and operation is better if the feed is predominantly UO_2 instead of higher oxides. The U(IV) is favorable to formation of UCl_4 while U(VI) allows excessive vaporizations of uranium as UCl_6.

Table 8. Properties of uranium oxide, UO_2-C, and carbon feed solids

Nominal composition	Description	Surface area (m^2/g)	Bulk density (g/cm^3)	Particle size (μm)
UO_2	Ball-milled powder	0.102	4.90	20–150[a]
UO_2	UO_3 gel spheres in H_2 to 740°C	7.37	1.3	300–500
UO_2-C C/U = 4.2 atom/atom	UO_3-C gel sphere in Ar to 740°C	30.52	0.80	400–800
C	Petroleum coke	1.34	1.15	50–400[a]
C	C-black for UO_2-C spheres	96.0[b]	0.2[b]	0.03[b]
C	Compacted C-black granules	c	0.68	100–1000[c]

[a]Some finer particles.
[b]Manufacturer's data.
[c]Probably ~100 m^2/g and 0.03 μm true basic particle size.

This effect has been reported for chlorinations using CCl_4, $COCl_2$ and other chlorination agents. The additions of uranium oxide feeds generally gave bursts of gas pressure that were largest for UO_3, smaller for U_3O_8, and smallest for feed that was nearly UO_2. Most of these chlorination tests have been with UO_2 feed even though the usual uranium ore concentrates are UO_3. Test MS-17 was made using a feed of UO_3 spheres to the UCl_4-carbon black charge remaining after test MS-16. The test was carried out to observe the UO_3-melt reactions and the chlorination reactions separately by adding the UO_3 without Cl_2 feed, and then starting the Cl_2 after the UO_3-melt reactions approached completion. The simplest and best result would be the reaction of UO_3 and carbon black to give UO_2, and then the same chlorination behavior after Cl_2 flow was started as for UO_2 feed. However, the reactions observed for UO_3 are much more complicated and less desirable than the simple reactions just mentioned. It appears the UO_3 also reacts with UCl_4 to form oxychlorides and that the U(VI) feed yields more UCl_6 than U(IV) feed. It is not certain exactly which reactions occur, but the observed results include the following:

1. The amount of CO_2 evolved before the start of Cl_2 flow was <15% of the total oxygen added as UO_3 (or about 40% of the oxygen for reduction to UO_2).

2. The amount of CO_2 evolved after the start of Cl_2 feed was much more than that for UO_2 and confirms that more than 85% of the oxygen introduced as UO_3 remains in the melt without reacting with the carbon until Cl_2 is fed.

3. The chlorine utilizations were only in the 50 to 70% range, while chlorine utilizations for the same conditions with UO_2 would have been ≥90%.

4. A plug of condensed uranium chlorides plugged the crucible cross section at the end of the test. This amount of condensed uranium chlorides was not expected based on results with UO_2 feed at similar conditions.

The chlorination reactions did not show any dependence on the physical properties of the uranium oxide feeds. The reactions of the uranium oxides with UCl_4 were rapid so that the availability of oxychlorides for oxidation by Cl_2 and reduction by C or CO did not vary with the physical properties of the uranium oxide feed. During test MS-22, batches of the ball-milled UO_2 of low-surface area and the uranium oxide gel spheres of high-surface area were alternated as feeds without any detectable differences in results. For either feed, the effects of the addition peaked as quickly as the feed addition was completed; both uranium oxides were available for reaction without any significant delay. The UCl_4 reacts with UO_2 to give $UOCl_2$, while higher oxides probably give mixtures of $UOCl_2$ and UO_2Cl_2.

The carbon and oxygen balances (Table 6) and the CO_2 collected per mol of Cl_2 reacted show consistent effects. The early tests with CO were commonly ended by reactor plugs before oxygen removal was complete. The extra oxygen in U_3O_8 or UO_3 as compared to UO_2 was noticeable. Exposures to air during shutdowns resulted in extra oxygen and loss of chlorine from the reaction of UCl_4 with water vapor.

The material balances as compared to the amounts of UO_2 feed commonly showed CO_2/UO_2 larger than 1 mol/mol, and Cl_2/UO_2 larger than 2 mol/mol. The excesses over the stoichiometric amounts would be expected from reactions of UCl_4 with water vapor during handling or from water, hydrocarbon, or oxygen impurities in the feeds. Any water in the feeds during chlorination would give both CO_2 and HCl that would collect on the first Ascarite trap, in addition to the CO_2 from chlorination of UO_2.

The effects of other impurities in the uranium oxide or the carbon have not been studied. Logically, some impurities would accumulate in the chlorination reactor melt. Other impurities would form volatile chlorides and be transferred with UCl_4 to the uranium metal product or transferred to the waste purge streams.

3.4 REDUCTIONS BY CARBON

Use of carbon as the reducing agent has important advantages over the use of CO. An excess of carbon remains in the melt ready for later use while an excess of CO separates and is lost to the exit flow of gases. The excess CO results in a toxic and flammable waste gas. The CO can react with excess Cl_2 to give $COCl_2$ (phosgene), which is more toxic than Cl_2 alone. Carbon feeds are easily stored and are commercially available in several forms while a large feed of CO would require special preparation or storage facilities.

The chlorination behavior using C and CO appears to agree with two thermodynamic concepts. An excess of solid carbon has an activity of one for chemical equilibriums. The CO is always diluted by other gases and has activities of less than one for atmospheric pressure. The free energies of formation for CO_2 and two molecules of CO are equal at 700°C. Because of the activities mentioned above and kinetic effects, some CO is possible from use of carbon at temperatures below 700°C.

The chlorination reactions in this study have shown better utilizations of chlorine and higher rates of reaction with carbon as compared to CO. The best steady-state utilizations of Cl_2 were 30 to 40% with CO feed, but Cl_2 utilizations were $\geq$90% for complete tests using carbon with some steady-state periods near 100%. Temperatures of $\geq$670°C were necessary for high Cl_2 utilizations using petroleum coke. The higher reactivity of carbon black was most clearly demonstrated during test MS-22. When the reactions appeared to be near steady state with 48 g of petroleum coke in the melt, an additional 2 g of carbon black was added. The rate of CO_2 formation doubled and the utilization of Cl_2 returned to nearly 100%. The peak in CO_2 evolution agreed with the amount of carbon black. A later addition of 2 g of petroleum coke did not give any noticeable change in CO_2 rate.

Another indication of the more rapid reaction of carbon black as compared to the petroleum coke is the more rapid decrease in CO_2 evolution after the Cl_2 feed is stopped. With melt temperatures over 700°C and carbon black, the CO_2 rate decreases almost immediately and rapidly. With petroleum coke, the CO_2 evolution may taper off over a 20 or 30 min period. This difference indicates that the petroleum coke results in a much higher inventory of U(VI) [or U(V)] that reacts with the coke over the 20 to 30 min period.

Rapid formations of CO_2 during chlorination were demonstrated with three types of carbon. A petroleum coke was used in the form of free-flowing, granular particles that were easy and clean to handle and feed. The frozen charge after cool down showed a floating bed

of salt-wetted coke particles. Carbon black dispersed in UO_2 gel spheres provided fine carbon particles of high surface area and very intimate mixing with the UO_2. The frozen change after cool down did not show any separation of carbon in the melt or as dust above the melt (the UO_2 dissolved in UCl_4). Test MS-1 was made at 850°C with a finned graphite cylinder as the source of carbon. The formation of CO_2 with little CO in spite of the 850°C temperature indicates a limited availability of carbon for reaction. Graphite shapes are not a practical carbon source for a production process. Either the petroleum coke or the carbon black mixed with UO_2 appear more practical. The carbon black gives high reaction rates at lower temperatures, otherwise, the choice probably depends on convenience of use, significance of impurities, and costs rather than the suitability of the compound as a reactant. A fine, dusty carbon black powder by itself might cause feeding problems, but carbon black is available as compacted granules.

3.5 REDUCTIONS BY CARBON MONOXIDE

The use of CO has the advantage of providing a highly pure reactant that is easily metered and fed. Excess reactant is easily separated from the reactor charge or from condensed products. However, these advantages are much less important than the high rates of reduction and the other advantages of carbon. With reduction by CO, utilization of chlorine was high for a short period only until U(IV) oxychlorides were mostly oxidized to U(VI). This condition gave much higher volatilities of uranium and poorer utilizations of Cl_2. It cannot be determined whether the chlorine escaped from the melt as Cl_2 gas or as UCl_6. The result was mostly condensed UCl_4 and losses of Cl_2 to the trap, but the UCl_6 might decompose to UCl_4 and Cl_2 in the condenser. This type of mechanism is discussed more completely in Sect. 3.6. From 75 to 90% of the CO feed left in the exit gases without reacting (Table 6). The limitation of CO can be summarized as follows:

> Using CO, the rate of reduction is lower, and it is difficult to avoid a charge that is highly oxidized by the Cl_2. This scenario is unfavorable with respect to chlorine utilization and the high volatility of uranium as UCl_6. With C as the reductant and good (high) concentrations of oxychlorides, the reduction reactions are much faster than reduction by CO so that the charge has higher concentrations of U(IV). This situation is favorable to good utilization of Cl_2. The lower U(VI) concentrations using C allow higher temperatures without excessive uranium volatility. The higher temperatures tend to give higher rates for both the chlorination and reduction reactions.

One test to expose materials of construction (MS-29) used both carbon black in the melt and CO with the Cl_2 gas feed. There was no detectable reaction of CO; all the reduction was apparently accomplished by the carbon black. The exit flow of CO did not vary for three Cl_2 feed rates (including no Cl_2 feed).

3.6 VOLATILIZATION AND CONDENSATION OF URANIUM CHLORIDES

During chlorination tests, major fractions and sometimes essentially all of the uranium is vaporized from the crucible and condensed outside the furnace. Examination of the condensed solids by X-ray diffraction shows the lines of UCl_4 only without any known lines of other uranium compounds. The published data indicate that the volatilities of uranium oxides and oxychlorides are negligible at the chlorination temperatures. However, the observed amounts of condensed solids are too large to agree with the vapor pressure of UCl_4 (Appendix).

The vaporization behavior of UCl_4 in the reactor without chlorine gas is consistent with the UCl_4 vapor pressure. There was no detectable condensed uranium from molten UCl_4 without a sparge gas (Test MS-11A). This fact indicates that a thermal convection cell is not a controlling means of vapor transport. With a nitrogen sparge, the amount of condensed uranium is small in approximate agreement with the vapor pressure of UCl_4 at the test temperature (Test MS-11B). With Cl_2 feed, the amount of condensed uranium is about five to ten times that calculated from the temperature and saturation of the noncondensable gases with UCl_4 vapor (test 11C and others) (Table 9).

The uranium condenses outside the reactor furnace and gives deposits of two distinctly different visual appearances. Both deposits show X-ray diffraction lines for UCl_4 only. The quartz reactor walls inside the furnace remain transparent and free of deposits throughout the chlorination tests. After a sparge flow is started, a haze of fine powder deposits on the quartz walls above the insulation. This deposit becomes opaque immediately above the insulating blocks in a short time and decreases in thickness to a partly transparent film in the cap. This type of deposit remains loose and powdery and can be discharged from a tilted reactor by moderate tapping or jolting. The color of the solids is the greenish-black of UCl_4 with some yellow-green tints for the deposits farthest from the furnace.

The other type of condensed solid is distinctly different in properties and appearance. This type of deposit forms the first 2 in. outside the reactor heated zone. The color is dark

Table 9. Gas flows and uranium volatilization[a]

Test No.	Furnace temperature (°C)	Flows out of crucible (mol)				Calculated UCl_4 vapor (mol)	Uranium condensed (mol)
		$CO + CO_2$	Cl_2	N_2	Total none-cond.		
4	625	0.31	0.20	0.1	0.61	0.02	0.04
7	655	0.70	0.56	0.21	1.47	0.005	0.006
8	645 680	0.60 0.60	0.86 0.86	0.27 0.27	1.73 1.73	0.13 0.13	0.44 0.44
9	645	0.10	0.25	0.11	0.46	0.02	~0.13
10A	645 680	0.14 0.14	0.29 0.29	0.50 0.50	0.93 0.93	0.027 0.040	~0.13 ~0.13
11C	635 690	0.12 0.12	0.33 0.33	0.61 0.61	1.06 1.06	0.022 0.022	0.13 0.13
12	635 680	0.30 0.30	0.23 0.23	0.56 0.56	1.09 1.09	~0.01 ~0.01	~0.01 ~0.01
13	680	0.20	0.30	0.52	1.02	0.024	~0.04
14	710	0.34	0.06	0.69	1.09	0.068	~0.05
15	745	0.28	0.30	0.46	1.04	0.21	0.15
16	705 675	0.45 0.45	0.06 0.06	0.52 0.52	1.03 1.03	0.09 0.09	~0.06 ~0.06
17	680	0.26	0.12	0.56	0.94	0.07	0.15
18	700	0.45	0.08	0.74	1.27	0.13	0.15
20	695	0.24	0.09	0.16	0.49	0.084	~0.28
21	677 699	1.03 1.03	0.17	0.30	1.50	0.24	~1.04
22	694 715	1.15 1.15	0.40 0.40	0.25 (3.00)[b]	1.80 (4.55)[b]	0.34 (0.85)[b]	0.68 0.68
23	731	1.00	0.75	0.5[b]	2.25	0.61	0

[a]Gas flows from start of Cl_2 feed until end of CO_2 evolution; CO, CO_2, and Cl_2 flows selected with weight material balances considered most accurate; charge temperatures were about 20°C lower than the furnace temperatures.

[b]Including UO_2 feed line purge N_2.

black-purple with a mirror surface against the quartz wall and coarse crystals on the inside of the reactor. These solids can completely plug the cross section to completely block gas flow. The deposits are dense and strong and fix the gas sparge tube in place so it cannot be withdrawn. The plugs can be broken into chunks by rodding and removed without breaking the quartz reactor. Removal of chunky deposits leaves a clean quartz wall while the powdery deposits of the other type do not.

Both types of deposits are found for all chlorination tests, but their rates of accumulation differ. A photograph for MS-8 shows both types of deposits and an almost complete vaporization of uranium compounds out of the crucible and heated zone (Fig. 4). The green-black powder deposits accumulate at moderate rates that increase with temperature in reasonable agreement with the vapor pressure of UCl_4. The dark, dense solids have highly variable rates of accumulation. The high rates occur at conditions that give higher losses of chlorine to the Cu trap in the off-gas cascade. The tests with CO as the reductant were most commonly ended by plugs of dark, dense deposits that restricted the gas flow before the intended run plan was completed. Some tests with carbon as the reductant were ended with only thin layers of the dark deposits on the quartz walls. The thin-layer result occurred only when the Cl_2 flow was stopped as soon as the off-gas flow rates indicated increased Cl_2 removal in the Cu trap.

The vaporization and condensation behavior is consistent with the following explanation. The vaporization of the uranium occurs as both UCl_4 and UCl_6. With an excess of carbon and oxychlorides in the charge, the steady-state concentration of U(VI) is low and the amount of UCl_6 vaporized is small. The chlorination gives an "oxidation" of U(IV) to U(VI). If the conditions for the reduction reaction are less favorable, the steady-state concentration of U(VI) and the amount of UCl_6 vapor increase. Conditions that lower the rate of reduction and thus increase the vaporization of UCl_6 are:

1. CO as the reductant (CO is less effective than carbon);
2. low concentrations of oxychlorides (inadequate UO_2 feed) as C or CO cannot reduce UCl_6 to U(IV); and
3. lower temperatures as the rates of reduction are more temperature dependent than the rates of chlorination.

The vapor pressures of both UCl_4 and UCl_6 increase with temperature. Nevertheless, the dark plugs of condensed solids were formed at some tests below 650°C while other tests at higher temperatures gave much less dark solids.

The experimental data do not explain how the UCl_6 vapor results in the deposit of dense UCl_4 solids. The thermochemical data indicate that a large partial pressure of Cl_2 is required to keep UCl_6 stable. Therefore, the UCl_6 might decompose to UCl_4 and Cl_2 as a surface catalyzed reaction. As an alternate explanation, the dark deposits may result from condensation at higher temperatures and higher UCl_4 concentrations while the powdery solids form at lower temperatures and lower UCl_4 concentrations.

The weight material balances for the large (68-mm-ID) reactor tests have given ten good measurements of uranium chloride vaporization for a range of conditions. The observed amounts of condensed solids have been compared with the calculated rates of UCl_4 vaporization. These calculations assume a UCl_4 vapor pressure given by an ideal melt of nonvolatile carbon solids and molten $MgCl_2$ and NaCl with the remainder of the charge as UCl_4. The N_2 sparge to the crucible and the CO_2 product are saturated with UCl_4 vapor at the melt temperature and composition. The results show agreement with the calculated results for the effects of temperature (i.e., UCl_4 vapor pressure), the effects of $MgCl_2$–NaCl as nonvolatile diluents, and the effects of N_2 sparge gas flow rates. However, the relative oxidation-reduction of uranium salts in the melt is also very important. The amounts of uranium vaporized compared to the calculated amounts of UCl_4 vapor without consideration of this factor have been as follows:

a. For no Cl_2 flows or for very small Cl_2 flows with good charges of carbon black, the experimental amounts have been less (80 to 100%) than the calculated amounts.

b. For the high Cl_2 and UO_2 feed rates with good charges of carbon black, the experimental amounts have been 100 to 150% of the caluclated amounts.

c. For useful Cl_2 flow rates and petroleum coke in the melt, the experimental amounts were about 300% of the calculated amounts.

d. Some tests in the small reactor system with CO as the reducing agent showed 500 to 1000% of the calculated amounts.

Chemical analyses of the deposited solids give little additional information. The UCl_4 is so reactive with water vapor (to form HCl) that sampling and analyses without oxygen contamination is extremely difficult. Reaction with O_2 to release Cl_2 is also possible, but the

rates are low below 100°C. As previously mentioned, x-ray diffraction shows lines for UCl_4 only without any lines for other uranium compounds. The chemical analyses for chlorine, total uranium, and U(IV) (Appendix B) showed small amounts of U(VI) and more chlorine than needed for UCl_4, but not enough to give all UCl_4 and UCl_6. It is believed that the difference is oxygen from reaction with water vapor during removal and sampling. In summary, the chemical analyses can be explained by deposits that are mostly UCl_4 with a small amount of UCl_6 and a small amount of reaction with water vapor to form oxychlorides before analysis.

Several of the plugs of dark, dense solids were melted and drained to the charge in order to allow continued chlorination. This operation was only possible when a tall crucible was used with the top extending above the insulation so the dark solid formed inside the crucible. The melting was done by either lowering the reactor into the furnace or by increasing the furnace temperature to over 800°C (this high temperature was necessary to give >600°C in the insulation above the furnace). A supplementary heater was procured for occasional use in melting plugs, but its use was not tested.

3.7 PRELIMINARY RESULTS WITH A LARGER REACTOR AND BOTTOM CONDENSER

After Test MS-18, the chlorination reactor was replaced with a reactor of larger (68-mm) diam designed to give a downflow of vapor and an additional flow of nitrogen diluent gas to a condenser at the bottom of the unit. The salt charge was in a crucible of 5.6 cm ID. The schematic flow sheet (Fig. 5) shows only small changes from that for the 4-cm diam reactor, but some flowmeters and reactors in the exit gas train are also larger. This larger system was operated to provide information on the condensation behavior of the uranium chlorides. The test conditions and results are included in the tabulations for the small reactor (Tables 1 through 6).

Tests MS-20 and MS-21 were with a charge of UCl_4 and C (petroleum coke particles) and UO_2 feed. Test MS-20 with 0.21 mol of UO_2 and moderate Cl_2 rates showed a steady accumulation of very dark gray-green solids falling to the bottom of the condenser chamber. Removing the bottom cap dropped 58 g of solids into a plastic sack (0.15 mol UCl_4 and an estimated 0.02 mol remaining in the condenser). Test MS-21 was made with 80 g/h of UO_2

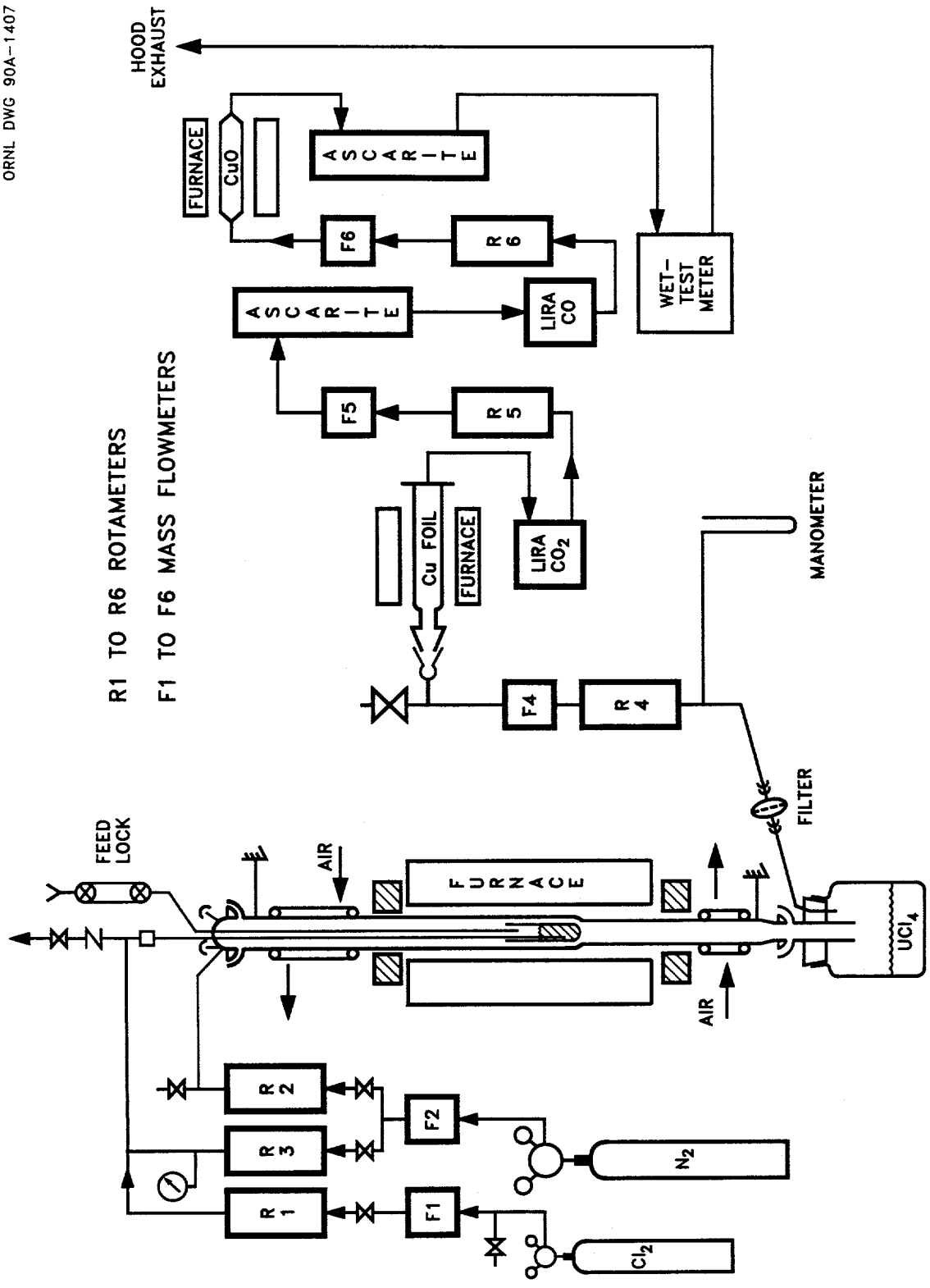

Fig. 5. Chlorination reactor (68-mm ID) with bottom condenser.

feed and gave 236 g of solids in a collection bottle below the condenser (0.62 mol UCl_4). The test went well with the exception of two plugs of feed lines for the UO_2 feed. The average Cl_2 utilization was 95% even though the chlorine feed was twice continued until the CO_2 showed a significant drop off from depletion of oxide from the charge.

After Test MS-21, the crucible was removed and the apparatus cleaned to obtain weight material balances for MS-20 and MS-21 together. The measured MS-20 and MS-21 results are:

- 1.47 mol UCl_4 in the initial charge;
- 4.5 mol C (petroleum coke) in the charge;
- 1.19 mol UO_2 fed to crucible;
- 1.27 mol CO_2 on traps;
- 2.8 (weight) or 3.3 (feed flowmeter) mol total Cl_2;
- 0.26 mol Cl_2 on Cu-foil trap;
- >90% Cl_2 utilization;
- 0.77 mol UCl_4 into product receivers;
- 0.38 mol UCl_4 released from the reactor walls by a wiper blade treatment;
- 0.09 mol UCl_4 remained on reactor walls;
- 0.12 mol UCl_4 deposits on cap, sparger tube, and feed tubes; and
- ~1.3 mol UCl_4 in the crucible after MS-21.

This discharge of UCl_4 powder as noncaking, flourlike particles shows a partial demonstration of the pilot plant product collection concept. Over 60% of the vaporized uranium discharged in this way, and 40% deposited on the apparatus walls. Part of the deposits were hard, dark, and difficult to loosen from the quartz wall. The 1.27 mol CO_2 compared to 1.19 mol UO_2 shows the effect of oxide impurities, water, or incomplete reduction of uranium oxides to UO_2.

Test MS-22 was like test MS-21 with the following changes:

1. additional charge to give about 10 cm depth of melt in the crucible;
2. addition of $MgCl_2$ and NaCl to give a charge composition (before reaction of UCl_4 with UO_2) of 1.7 mol UCl_4, 0.21 mol $MgCl_2$, and 0.21 mol NaCl;
3. a large purge flow of nitrogen to the UO_2 feed line and a reduced nitrogen purge flow into the reactor top; and
4. several different UO_2 feeds to observe the differences in exit gas rates and composition vs the feed characteristics.

Test MS-22 gave results that are favorable with respect to steady-state operation. The chlorine feed was maintained for 4 h at 0.01-mol Cl_2/min and an overall chlorine utilization of 82%. Flow differences indicate an initial chlorine utilization of near 100% for 1 h. After the flow differences showed a decrease in chlorine utilization, a feed addition containing 2 g of carbon black gave a short period of doubled CO_2 evolution and a return to near 100% chlorine utilization. These increases indicate that the conversion was limited by the reaction of the petroleum coke and that the addition of 2 g of carbon black to the charge containing 48 g of petroleum coke more than doubled the rate of the reduction reaction. After the chlorine utilization had again dropped, an additional 2 g of petroleum coke did not yield a significant change (<10%) in the rate of CO_2 evaluation. The nitrogen purge to the UO_2 feed line eliminated the plugs or deposits that occurred in Test MS-21 without a purge. There was no observable difference in reaction results for dense UO_2 of low surface area (ball milled), as compared to porous UO_2 of high-surface area (gel process spheres). The condensed uranium was again divided about 60% as discharged powder and 40% as deposits on the reactor walls in agreement with tests MS-20 and MS-21 results. The moles of condensed uranium was 65% of the feed UO_2 as compared with about 115% for Tests MS-21 and MS-22. The lower amount of uranium vaporized agrees with previous results showing less volatility of uranium with $MgCl_2$ and NaCl in the charge. The deposit of dense dark crystals on the reactor wall at the low end of the furnace was much smaller for Test MS-22.

Test MS-23 was intended to test a more steady-state operation using a combination of UO_2-C spheres and UO_2 powder to give a feed UO_2/C ratio of 1 mol/mol. Test MS-23 run schedule was completed as planned with the exception of a severely restricted gas flow inside the quartz reactor just after the chlorine feed was shut off. A quartz baffle with nitrogen flow to the reactor top completely eliminated the deposition of condensed uranium above the furnace. The total UO_2 added and reacted (0.15 mol prerun and 0.96 mol at temperature) was greater than any of the previous tests. The quartz crucible probably cracked during heatup and leaked part of the charge into the bottom region of the reactor. The frozen melt probably obstructed the vapor flow to the condenser and affected the other test results.

Tests MS-24 through MS-30 were intended to provide information important to the design of pilot-plant chlorination equipment. A series of tests were completed to determine results for short-term steady-state operation with increasing rates of UO_2 and Cl_2 feed (see Table 7). The Cl_2 feed rates were up to 770 cm^3/min (34 mmol/min) for test MS-26, and

1030 cm^3/min (46 mmol/min) for test MS-28. Test MS-28 demonstrated a continuous screw feeder for UO_2 powder, while all previous tests were run with periodic batch additions of UO_2. The primary objective of tests MS-27 and MS-29 was to expose three proposed materials of construction (carbon composites) to the chlorination reactor conditions. The MS-27 and MS-29 results also give chlorine utilizations at low chlorine feed rates for comparison with the higher rates. The vaporization and condensation behavior of the uranium chlorides was observed for a wide range of Cl_2 feed rates and some variations in the gas and vapor flow configurations. The most favorable reaction conditions of carbon black in the melt and melt temperatures over 700°C were used, with the exception of a lower temperature for MS-30.

Many of the MS-24 – MS-30 results are included where appropriate in Sects. 3.2 – 3.5. The tests of material specimens were part of a larger investigation and are reported elsewhere.*

A primary criteria for design and operation of the larger reactor system was to provide a separate condensation and measurement of the condensed uranium compounds. The simplest model for the vaporization behavior is that the gases leaving the melt are saturated with UCl_4 at the melt temperature. The results for MS-4 through MS-18 commonly show much larger amounts of volatilized uranium—often five to ten times the amounts calculated from the UCl_4 vapor pressure. These results are discussed and an explanation suggested in Sect. 3.6. The results for MS-20, -21, and -22 with petroleum coke show condensed solids about three times the amounts calculated from the vapor pressure of UCl_4. The utilizations of Cl_2 and the results from a small addition of carbon black in MS-22 indicate a need for better reductions of U(VI) [or U(V)] to U(IV). By using carbon black in melts at >700°C, the amounts of condensed uranium were much closer (typically 120%) to that calculated for the UCl_4 vapor pressure. The high chlorine utilizations (see Sect. 3.2) are consistent with this change in vaporization behavior.

Discharge and collection of a UCl_4 powder are highly desirable to avoid the problems from deposition of UCl_4 solids or the problems of collecting a UCl_4 liquid product. The proposed plant concept is to use a quench gas recycle to produce solids below the UCl_4 triple point of 15 mm Hg, 590°C. Our reactor system does not allow the large gas flows necessary for a valid test of this concept. The MS-20 to MS-30 results show 48 to 73% of the condensed uranium as powder into the product jar and 27 to 52% deposited on the system walls. The two most important effects on how the condensed solids collected appeared to be:

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*To be issued as an AVLIS program milestone report approximately September 1991.

1. Turbulence in the condenser results in deposit of condensed UCl_4 on the walls and reduces the fraction that discharges to the product jar. A quench gas inlet into the condenser gave poor results.

2. More dilution of the UCl_4 vapor increases the fraction of solids discharged, but the dilution must be done without turbulence in the condenser. The highest Cl_2 feed rates gave the highest UCl_4 vapor concentrations (230 mm of Hg calculated) and deposits that completely closed the condenser cross section.

4. CONCLUSIONS

High rates of chemical reaction and good utilizations of Cl_2 were demonstrated for reaction of UO_2, Cl_2, and C to produce UCl_4. A molten salt medium containing UCl_4 allows dissolution of UO_2 by the reaction $UO_2 + UCl_4 \rightarrow 2UOCl_2$, and this is favorable to high rates of reaction. Starting with UO_2 dissolved in UCl_4, the initial rates of reaction of chlorine can be very high with low concentrations of chlorine in the exit gas. The rates of reduction reactions to remove oxygen as CO_2 or CO control the overall rates of UCl_4 formation. With carbon black in a melt at about 730°C, the rates of CO_2 evolution matched the Cl_2 rates for Cl_2 feed rates up to 0.046 mol/min in a crucible of 5.6-cm ID.

Less favorable conditions for reduction give lower utilizations of Cl_2 at steady state and greater volatilization of uranium—probably as UCl_6 or UCl_5. Carbon black gave practical rates of reaction and good results for melt temperatures down to 645°C. Petroleum coke of low-surface area gave poorer results at 730°C than carbon black at 645°C. With CO as the reducing agent, the steady-state utilizations were <40% for Cl_2 and 10 to 25% for CO.

The uranium oxide should be reduced to approximately UO_2 before use as chlorination feed. The results indicate that the chlorination reactions are simpler and operation is better for UO_2 as compared to U_3O_8 or UO_3. A test with UO_3 feed gave lower chlorine utilizations and much more condensed uranium than for UO_2 feed at similar conditions. The physical properties of the UO_2 feed do not appear to be important; UO_2 feeds of low- and high-surface areas did not show any detectable differences in results.

The amounts of condensed uranium were compared with calculated rates of UCl_4 vaporization. The calculations assume that the N_2 sparge to the melt and the CO_2 product are saturated with UCl_4 vapor at the melt temperature and composition. The results showed agreement with the calculated results for the effects of temperature (i.e., UCl_4 vapor pressure),

the effects of $MgCl_2$-NaCl as nonvolatile diluents, and the effect of the N_2 sparge gas flow rate. However, the relative oxidation-reduction of uranium salts in the melt is also very important. The experimental amounts were from 80 to 150% of the calculated amounts with good reducing conditions (carbon black or no Cl_2), but were from 300 to 1000% of the calculated amounts for chlorinations with petroleum coke or CO reducing agents.

The experimental system used here did not allow a valid duplication of a pilot-plant collection system for UCl_4 vapors. From 48 to 73% of the condensed solids were collected as a powder in a product jar below the condenser; the other 27 to 52% deposited on the apparatus walls. The deposits on the walls were partly powder and partly dark, dense crystalline solids that formed more rapidly when the Cl_2 feed rate exceeded the rates of reduction reactions. Examination of both types of solids by X-ray diffraction shows the lines of UCl_4 only without any lines of other uranium compounds. Chemical analyses for uranium and chlorine indicate mostly UCl_4 with small amounts of UCl_6, and probably some oxychlorides from reaction with water vapor during sampling.

Control of the UO_2 feed rate to the chlorination melt is very important to dependable, steady-state operation. A deficiency of UO_2 results in poor utilizations of Cl_2 and much higher (excessive) volatility of uranium. The UO_2 feed reacts rapidly with UCl_4 to give $UOCl_2$, which has a limited solubility in the molten chloride salts. Excessive UO_2 can solidify the charge so that the gas flow is obstructed or channels with poor contact. Carbon particles are wetted by and remain suspended in the melt; a wide range of carbon black inventories is acceptable. When the reduction conditions are favorable, all reaction rates are determined by the Cl_2 feed rate.

Overall, good results were demonstrated for the chemical reactions to produce UCl_4 from UO_2, Cl_2, and carbon black. This result is much different than the results of an earlier study to prepare uranium metal by electrolysis of UO_2 dissolved in fluoride salts. There, chemical reactions other than the desired ones always resulted in reductions of UF_4 in addition to UO_2 and in low current efficiencies. The engineering problems for UCl_4 preparation (materials of construction, process control, UO_2-C, and Cl_2 feed procedures, UCl_4 condensation and removal) can be addressed in pilot-plant systems with confidence in the chemical flow sheets for the process.

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APPENDIX

A. THERMOCHEMISTRY

A. THERMOCHEMISTRY

The use of thermochemical data does not identify the probable reactions with any certainity or degree of confidence. There are several major causes of uncertainty. Uranium chemistry is complex with stable valences of 3, 4, 5, and 6, and with stable oxychlorides. UO_2Cl_2 and $UOCl_2$ are well-known compounds and others are possible. All the possible products must be considered. The uranium chlorides are more volatile with increasing valence, but UCl_5 and UCl_6 are less stable with increasing temperature and decreasing Cl_2 partial pressure. All the uranium compounds have large heats of formation, and calculating the free energy of these reactions usually results in a small difference from two large numbers. Small percentage uncertainties for the large numbers give large uncertainties for the differences.

Thermochemical data (Table 10) can be used to make calculations for chlorination reactor conditions.[10-12] A temperature of 700°K (427°C) is about the lowest temperature of interest for practical rates of reaction, and the 1100°K (823°C) is above the boiling point of UCl_4 and is near the highest practical temperature. The relationships between the different U-O-Cl compounds can be illustrated by a matrix listing (Tables 11 and 12).

Data are available for heats of formation at 298°K for all the compounds (Table 11). The free energies of reaction of 900°K are more useful for the calculations (Table 12), but the data are much less complete. Table 12 shows estimated values for some of the compounds and one of several different published values for UO_2Cl_2.

Tables 11 and 12 appear to show that the oxychlorides are more stable than either the chlorides or oxides. The free energies of formation show that either the U(VI) chloride or oxide are easily reduced to the corresponding U(IV) compounds, but the U(VI) oxychlorides are more difficult to reduce to U(IV) compounds. Since the oxychlorides are probable intermediates for conversion of uranium oxides to uranium chlorides, a conversion may appear favorable overall, but one of the steps involving an intermediate may be much less favorable. For example, consider the following:

$$UO_2 + 2C + 2Cl_2 \rightarrow UCl_4 + 2CO\ .$$

At 900°K, ΔG = -246.5 kJ, but individual steps show:

$$UO_2 + Cl_2 \rightarrow UO_2Cl_2, \quad \Delta G = -174.2;$$
$$UO_2Cl_2 + C \rightarrow UOCl_2 + CO, \quad \Delta G = 13.6;$$
$$UOCl_2 + Cl_2 \rightarrow UOCl_4, \quad \Delta G = -119.8; \text{ and}$$
$$UOCl_4 + C \rightarrow UCl_4 + CO, \quad \Delta G = 34.1\ .$$

Table 10. Thermochemical data

Compound	Melting point (°K)	Boiling point (°K)	Free energy of formation, -ΔG° (kJ/mol) 700°K	900°K	1100°K	Ref. No. for data
Cl_2	172.	238	0	0	0	10
CCl_4	250.	350	-1.7	-28.3	-54.6	10
$COCl_2$	169.	281	187.1	177.8	168.7	10
CO_2	216.	195 (subl)	395.4	395.7	396.0	10
CO	74.	81	173.5	191.4	209.1	10
C_s	—	>4000	0	0	0	10
$UCl_{3\,s}$	1115	—	741.8	699.1	656.5	11
UOCl	—	—	~715.	—	—	13
UCl_4	863.	1065	847.8_s	794.5_l	751.0_l	11
$UOCl_2$	a	—	943	900	857	11
UO_2	3150	—	963.5	930.8	897.7	12
UCl_5	600	800	845.3	~780	~723	11
$UOCl_3$	—	—	—	—	—	13
UO_2Cl	—	—	—	—	—	13
$1/3[U_3O_8]$	d-1300	—	1038.0	998.1	958.2	12
UCl_6	452	~550	841.3	789.3	~747.	11
$UOCl_4$			—	—	—	13
UO_2Cl_2		>1050	1130	1105	1080	13
UO_3	a	—	1043.0	992.9	942.3	1

[a]Decomposes.

Table 11. Heats of formation for U-O-Cl compounds at 298°K
- $\Delta_f H°$ in kJ/mol U

Reference No.: See Table 1 for Compounds

Valance	All Cl	One O	Two O	>Two O
0	U 0	U 0	U 0	U 0
3	UCl_3 893.3[a]	UOCl 947.3		
4	UCL_4 1051.4	$UOCl_2$ 1087.8	UO_2 1083.7	
5	UCl_5 1094.1	$UOCl_3$ 1185.7	UO_2Cl 1188.3	
5.33 or 5.5			$(UO_2)_2Cl_3$ 1202.5	U_3O_8 1191.2
6	UCl_6 1132.6	$UOCl_4$ 1238.5	UO_2Cl_2 1247.3	UO_3 1225.9

[a]Values of 860 to 880 kJ/mol are also reported.

Table 12. Free energies of formation for U-O-Cl compounds at 900°K (627°C)
- $\Delta_f G$ in kJ/mol U

Valance	All Cl	One O	Two O	>Two O
0	U 0	U 0	U 0	U 0
3	UCl_3 699.1	UOCl ~780 est.		
4	UCL_4 794.5	$UOCl_2$ 900.2	UO_2 930.8	
5	UCl_5 780	$UOCl_3$ ~1000 est.	UO_2Cl ~1000 est.	
5.33 or 5.5			$(UO_2)_2Cl_3$ ~1050 est.	U_3O_8 998.1
6	UCl_6 789.3	$UOCl_4$ ~1020 est.	UO_2Cl_2 1105	UO_3 992.9

These numbers indicate that the reactions could stop at UO_2Cl_2 or $UOCl_4$. If using CO to give CO_2 as the product is considered, then the two reduction reactions change to:

$$UO_2Cl_2 + CO \rightarrow UOCl_2 + CO_2, \quad \Delta G = 0.5 \text{ and}$$

$$UOCl_4 + CO \rightarrow UCl_4 + CO_2, \quad \Delta G = 21.2 .$$

The uncertainties for $\Delta_f G°$ values of UO_2Cl_2 and $UOCl_4$ are probably larger than either of the above ΔG values, so it is difficult to determine whether the reactions are thermodynamically favorable. The more favorable calculation for CO as compared to C may also be misleading. The C would be present as a solid with an activity of 1, while CO would be mixed with other gases and would have a lower activity for 1 atm total pressure.

Many of the reactions to change between the U-O-Cl compounds are shown in Fig. 1. Large values for the negatives of the free energies of reaction (kJ/equiv at 900°K) show reactions that are thermodynamically favored. Negative values in Fig. 1 indicate that the reactions are not thermodynamically favorable. The data for the oxychlorides are uncertain and values ranging from -20 to +20 kJ do not justify predictions. The formation of UCl_5 and UCl_6 appears to require excesses of Cl_2 and will not be complete. Otherwise, all additions of Cl_2 are favorable and oxychlorides should add chlorine to give UO_2Cl_2 or $UOCl_4$. The reduction of UO_3 or U_3O_8 to UO_2 by CO are highly favorable. The reduction of $UOCl_3$ by CO to give UCl_3 is very unfavorable. The other three reductions of oxychlorides by CO give free energies of reaction that are too near zero to justify predictions. A practical preparation of UCl_4 probably requires that the reductions of UO_2Cl_2 and $UOCl_4$ are possible as they would otherwise accumulate as stable products. Some additional possible reactions not shown by the diagram include:

$UCl_4 + UO_2 \rightarrow 2UOCl_2, \quad \Delta G = -74.7$ kJ;
$UCl_5 + UO_2Cl \rightarrow 2UOCl_3, \quad \Delta G = \sim -220$ kJ;
$UCl_6 + UO_2Cl_2 \rightarrow 2UOCl_4, \quad \Delta G = \sim -145$ kJ;
$UCl_4 + UO_2Cl_2 \rightarrow 2UOCl_3, \quad \Delta G = -100$ kJ;
$UCl_6 + UO_2 \rightarrow UO_2Cl_2 + UCl_4, \quad \Delta G = -179$ kJ; and
$UCl_6 + UOCl_2 \rightarrow UOCl_4 + UCl_4, \quad \Delta G = -125$ kJ .

The first five reactions indicate that the uranium chlorides will react to give oxychlorides.

Krahe listed vapor pressure equations as shown in Table 13.[14] Calculated values from these equations are shown as Fig. 6 The decomposition of UCl_5 (or UCl_6) into Cl_2 and UCl_4 must also be considered as the UCl_5 or UCl_6 are only stable when excess Cl_2 is present.

Table 13. Vapor pressure equations[a]

Compound	A	-B	-C	Temperature (°K)
UCl_3 (s)	19.224	15,760	3.02	298 - 1110
UCl_3 (l)	24.044	14,340	5.03	1110 - 1950
UCl_4 (s)	20.329	11,350	3.02	298 - 863
UCl_4 (l)	26.079	9,950	5.53	863 - 1062
UCl_5 (s)	21.810	7,450	4.03	298 - 600
UCl_5 (l)	26.027	6,210	6.29	600 - 800
UCl_6 (s)	22.317	4,765	5.03	298 - 453
UCl_6 (l)	26.120	4,060	7.04	453 - 650

[a] $\log p_{atm} = A + B/T + C \log T$

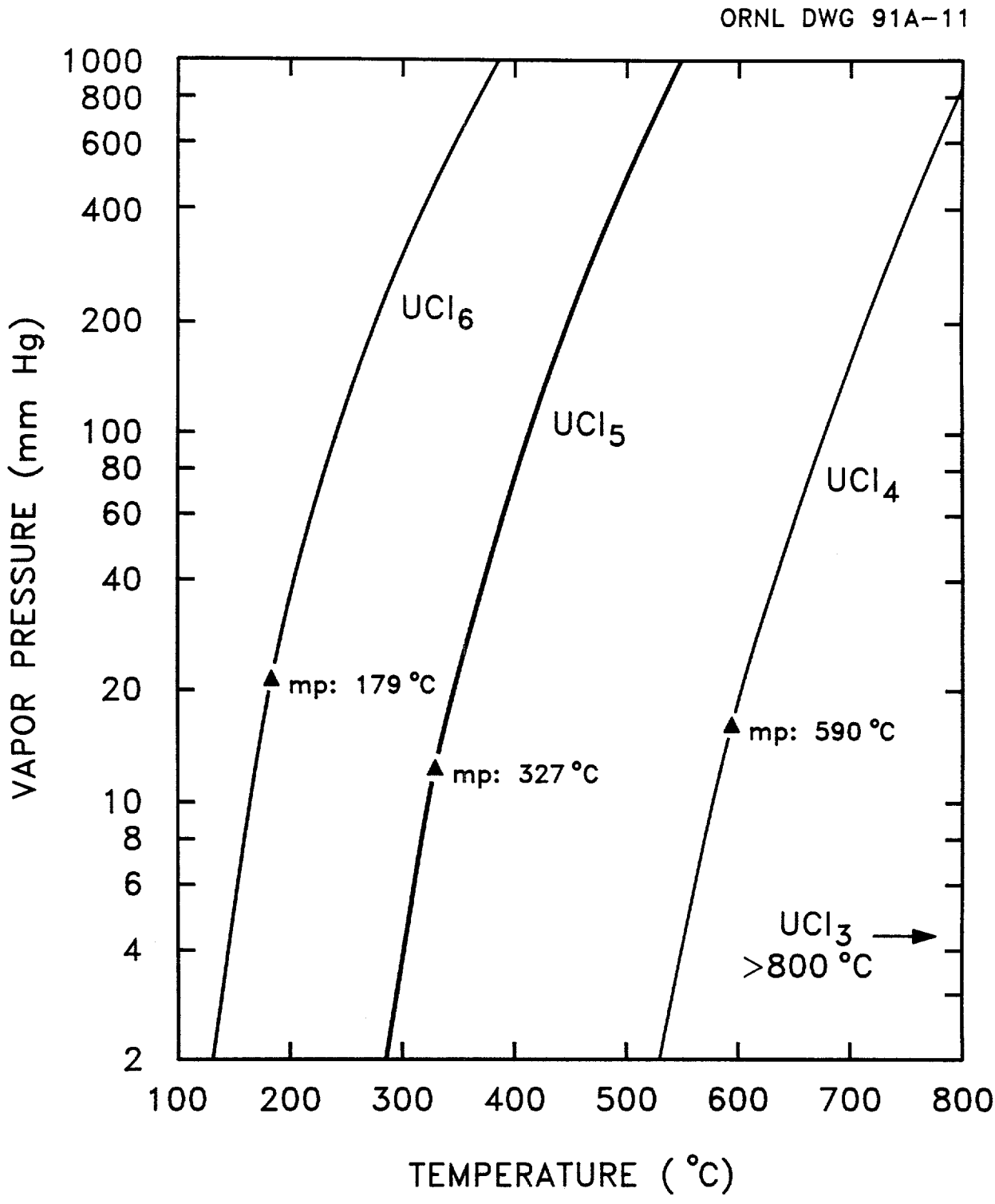

Fig. 6. Vapor pressures of uranium chlorides.

B. INDIVIDUAL TEST RESULTS

Some detailed results are given here as examples of the experimental studies. Some tests are not mentioned to minimize duplication or for the following reasons:

- MS-1, MS-2, MS-3, MS-4—details are in a preliminary report.[3]
- MS-5, MS-9B—mechanical failures; therefore, no useful chlorination results.
- MS-6, MS-19—training and calibration tests without any uranium or salt charge.
- MS-11A, MS-11B—volatility tests without chlorine feed.

B.1 MS-8

Test MS-8 was made with a charge of 103.5 g UCl_4 and 50.0 g of UO_2 and other conditions similar to MS-4. The Cl_2 flow was started with an estimated sparger immersion of half of the melt depth as greater immersions resulted in zero gas flow. A good flow of CO_2 was indicated in 10 min in agreement with the system holdup times. This CO_2 evolution peaked in 30 min and tapered off to about half the peak value by 60 min. The CO_2 evolution rate continued for 3 h with only small effects from increased immersions of the sparger, a 30°C temperature increase, and changes in Cl_2 feed rate. After 4 h of Cl_2 feed, the chlorination reactor plugged and would only pass about 20% of the intended gas flow even though the feed gas pressure was increased to 6 psig. Disassembly of the cold system showed a complete closure of the reactor cross-section by a dark crystalline dome of solids above the furnace, but below the cooling jacket (Fig. 4). The sparge tube and the thermowell were frozen in position by the solids. The upper half of the solid deposits were a loose powder instead of dense crystals. The crucible and reactor bottom only contained a few crumbs of solids.

A simple plug flow of gases that are saturated with UCl_4 cannot account for the transfer of uranium solids. The total amount of gas feed was about 1.6 mol to give a calculated UCl_4 concentration of 20 to 25 mol % in the vapor. The UCl_4 vapor pressures are reported to be 60 and 110 mm Hg at the two run temperatures of 650 and 680°C.

The rate of CO_2 evolution showed little variation with run variables (temperature, sparger immersion, Cl_2 flow rate, crucible charge depletion). The CO rate was approximately constant throughout the test.

The results of the MS-8 material balances are:

Weight measurements show:

Feed UCl_4	103.5 g, 0.272 mol U, 0.544 mol Cl_2.
Feed UO_2	50.0 g, 0.185 mol U, 0.370 g-atom O_2.
Cu Trap	42.2 g Cl_2 or 0.592 mol Cl_2.
1st Ascarite	8.7 g CO_2 or 0.198 mol CO_2.
CuO	-5.9 g O_2 or 0.369 g-atom O_2.
2nd Ascarite	16.2 g CO_2 or 0.368 mol CO_2 or CO.
Chlorination Reactor	15.3 g weight gain or 18.7 g Cl_2 (allowing for O_2 loss) to give 0.264 mol Cl_2 reacted.

Gas flow rates times concentrations show:

About 0.45 mol CO feed (vs 0.57 mol CO_2 on Ascarite traps),
About 0.9 mol Cl_2 feed (vs 0.86 volume from weights),
0.23 mol CO_2 (vs 0.20 on trap), and
0.45 mol CO (vs 0.37 on trap).

Differences in flow rates show:

0.42 mol CO, a good check;
0.22 mol CO_2, a good check;
0.68 mol CO + CO_2, a reasonable check; and
From 0 to 0.6 mol Cl_2 to CU trap, depending on which flow measures are used.

Chemical analyses of product samples show:

97.2% of feed uranium,
110% of calculated Cl_2, and
19% of calculated O_2.

Calculated compositions of:

	Dark crystalline solids, mol %	Powdery solids, mol %
UCl_4	93.8	81.4
UO_2Cl_2	0.9	10.8
UCl_6	5.3	7.8

Examination of the two solids by X-ray diffraction show only UCl_4 with no indication of other uranium compounds.

B.2 MS-22

Material was added to the crucible removed after MS-21 (541.7 g of charge, 7-cm depth) as follows:

- 20.0 g $MgCl_2$,
- 12.0 g NaCl,
- 12.0 g C (petroleum coke),
- 60.0 g UO_2 (ball-milled powder), and
- 42.5 g UCl_4 (the condensed MS-21 wall deposits).

The reactor furnace was controlling at 685°C at 10:30 a.m., but the sparger appeared to show solids and signs of plugging when lowered to less than 2 cm from the crucible bottom. The Cl_2 flow was started at 10:55 and 20 g batches of UO_2 feed added at 11:35 and at 15-min intervals thereafter with some omissions. The sparger was lowered to the crucible bottom at 11:18 a.m. with no signs of solids or plugging. The evolution of CO_2 is shown by the recorder chart for the CO_2 concentration (Fig. 7) and were confirmed by post-run gas flow calculations (Table 14). After 1 h with little or no flow differences for flows in and out of the Cu trap for Cl_2, these flows appeared to show chlorine losses. At 13:10, 10 g UO_2 – 2 g carbon black was added. This resulted in a very high rate of gas evolution that overpressurized the gas train and showed about triple the previous CO_2 rate. This high rate decreased back to the base rate in about 20 min. The remaining UO_2 feed additions and an addition of 2 g of petroleum coke were completed without any noticeable effects on the CO_2 concentrations or rates. About 45 min after the last UO_2 feed, the CO_2 rate decreased sharply and the Cl_2 losses increased, indicating a depletion of oxide from the charge. The Cl_2 feed was stopped and the CO_2 rate decreased to a low value in about 30 min.

After cool down, the weights showed:

- +31.2 g or 0.44 mol Cl_2 on the copper trap;
- +47.9 g or 1.089 mol CO_2 on the 1st Ascarite;
- ~0 g or ~0 mol CO oxidized by the CuO;
- +0.8 g or 0.018 mol CO_2 from CO on the second Ascarite trap;
- 134.1 g or 0.353 mol UCl_4 powder in the product jar;
- 66.1 g or 0.174 mol UCl_4 collected by scraping the reactor walls;
- 0.29 g or <0.001 mol UCl_4 on the filter;
- 838.4 g of charge in the crucible as about 10.5 cm depth of melt; and
- 37 g or 0.097 mol of UCl_4 collected by washing the reactor, the cap, sparger, and feed line.

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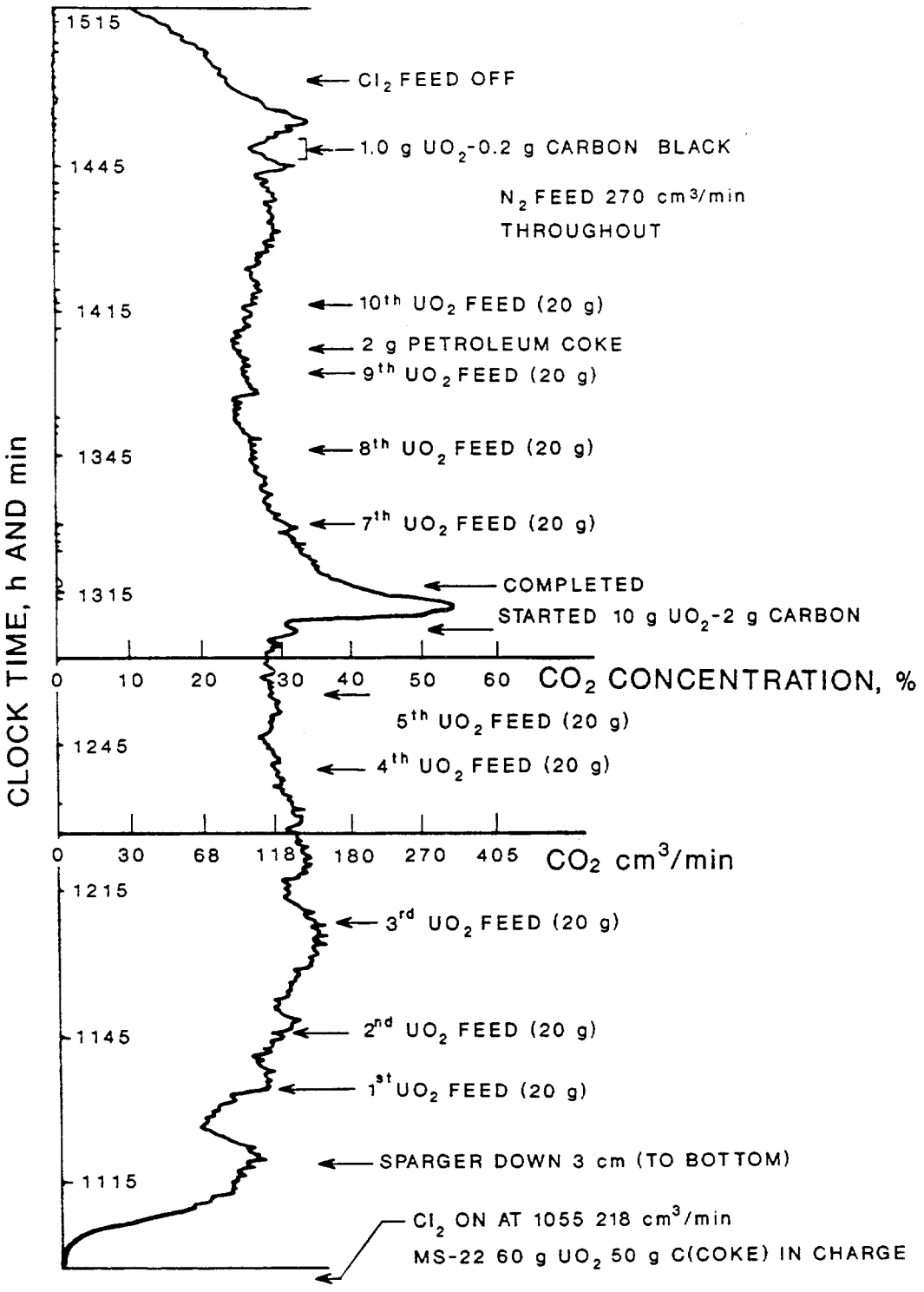

Fig. 7. CO_2 concentrations during MS-22.

Table 14. MS-22 gas flow calculations from totalizer readings

Clock times	Δt (min)	Comments	Calculated gas flows, cm^3 of N_2 equiv							
			Meters, gas, and meter factors							
			Wet test N_2	FM-2 N_2	FM-6 N_2 + CO	FM-1 Cl_2	FM-4 N_2 + CO + CO_2 + Cl_2	FM-4 minus FM-5 Cl_2 on Cu	FM-5 N_2 + CO + CO_2	FM-5 minus wet test CO_2 + CO
			1.00	1.01	1.20	1.21	1.17	--	1.40	--
0900	45	Heatup	19,800	18,350	13,000	0	20,830	800	20,030	230
1015	30	No Cl_2	7,010	7,950	7,920	0	8,000	0	8,270	1,260
1045	15	Cl_2 on 1055	4,290	4,010	4,500	1,170	4,240	0	4,340	50
1100	15		4,700	3,990	4,680	3,810	5,640	0	5,700	1,000
1115	15		3,800	3,910	4,140	3,870	5,440	0	5,530	1,730
1130	31	Two UO_2 feeds	8,270	8,030	8,180	8,020	13,400	450	12,950	4,680
1201	29	One UO_2 feed	7,680	7,590	7,660	7,500	13,130	460	12,670	5,020
1230	30	Two UO_2 feeds	8,030	8,280	8,100	7,940	13,244	770	12,470	4,440
1300	21	UO_2-C, gas loss	5,440	5,800	~5,500	5,340	9,750	240	9,510	4,070
1321	9		2,200	2,430	~2,000	2,070	3,700	0	3,750	1,550
1330	30	Two UO_2 feeds	8,170	8,210	8,100	7,540	12,285	0	12,290	4,120
1400	32	Two UO_2 feeds	8,860	8,830	9,220	8,110	13,570	552	13,020	4,160
1432	23		6,450	6,310	6,070	5,783	10,470	800	9,670	3,220
1455 1531	36	Cl_2 off 1503	8,980	9,990	8,210	1,900	12,050	560	11,490	2,510
Whole run	391		103,680	103,680	106,000	63,065	145,750	4,014	141,736	38,056
Corrected to true gas			103,680	103,680	106,000	53,605	--	3,410	--	27,780
Avg. flow (cm^3/min)			265	265	270	217 (247 min)	373	--	362	112 (247 min)

The flowmeter totalizer readings and the average of pre- and post-run calibration factors were used to calculate flows for fourteen intervals (Table 14). There were some losses of gases to allow breakup of a cake on the top of the 1st Ascarite absorber at 12:10 p.m., and from the overpressurization at 1:10 p.m.

B.3 MS-28

Test MS-28 was made using a continuous feeder for UO_2 powder and Cl_2 feed rates of 620, 840, and 1030 cm^3/min. This feeder is a glass and Teflon unit with a screw of Teflon flights inside a glass tube and a closed, gas-purged hopper. The screw uses an O-ring seal and gives controlled and reproducible powder feed rates using a variable-speed drive motor. The powder bridged in the hopper above the screw several times, but the bridges were easily seen through the glass and were broken by moderate taps on the hopper wall. Feed was interrupted twice by plugs at the end of the feed tube in the chlorination reactor. These plugs were hard, tight solid cylinders in the last 0.5 cm of the feed tube and appeared to result from reaction of condensed UCl_4 with UO_2. After the second plug, the feed tube end position was changed to about 1 cm into the crucible instead of 4 cm; the test was then completed without further feed difficulty. The tube end was partly restricted by solids when removed after cooldown.

Test MS-28 was made in three parts as a result of the two replacements of plugged feed lines. Nitrogen purge gas was lost during these replacements and through a leak early during the test, but all other material balances were excellent. The weight balance showed 0.1% loss, and the weights were confirmed by the flow rates times concentrations and by the flow differences. The overall results included:

UO_2 feed	521 g (1.93 mol)
Product jar	390 g (1.03 mol)
Reactor wall deposits	432 g (1.13 mol)
Cu trap	22.0 g (0.310 mol Cl_2)
Other traps	103 g (2.34 mol CO_2)
Total Cl_2 feed	316 g (4.46 mol Cl_2)
Average Cl_2 utilization	93.1%

The reactor wall deposits included a nearly complete closure of the reactor cross-section by deposits between 2 and 5 cm below the bottom end of the furnace. This is inside the end insulating brick and just above the cooling jacket. The deposits were about 50% removed as powder by moderate scraping, 35% hard, dense chunks removed with difficulty, and 15% as thinner films removed by water washes. The product jar collection was 53% of the UO_2 feed or 48% of the condensed solids.

C. EQUIPMENT DETAILS AND CALIBRATIONS

This equipment used quartz as the material of construction for hot chlorine gas. The components in contact with chlorine gas at room temperature were also selected to avoid excessive corrosion. Otherwise, the system was a series of small, special chemical reactors and commonplace types of laboratory flowmeters, temperature measurements, and control instruments.

C.1 Flow Control and Measurement

Feed flows of gases were set manually using needle valves and variable area flowmeters with ball floats. The primary flow measurements for material balances were the totalizer readings from Hastings mass flowmeters. One-time readings of indicators were not accurate for material balances because of delayed effects of both melt and gas inventory changes, a resonance-type oscillation of exit gas flows, and drifts of feed flows between flow adjustments.

The flowmeters were calibrated with N_2 having one primary calibration at the ORNL instrument shop, and secondary calibrations against the wet-test meter just before or after experimental tests. The Hastings mass flowmeters exposed to Cl_2 (F1, F4, F5) showed continuing changes in calibration. The long-term change was to require an increasing multiplier to convert the indication to a true flow, but there were also some short-term decreases in multipliers. The calibrations remained linear; the multipliers were time dependent, but not flow dependent. The manufacturer's factors were used to convert the indicated nitrogen flows to other gases. These were the following (air = 1.00) for the mass flowmeters.

Gas	Conversion Factor
N_2	1.02
CO	1.00
CO_2	0.73
Cl_2	0.85

The material balances were based on the N_2 equivalents being additive. For example, a combined flow of one liter each of N_2, CO_2, and Cl_2 would show as 1(1.02/1.02) + 1(1.02/0.73 + 1(1.02/0.85) = 3.60 L on the totalizer.

The variable area flowmeters were convenient for short-term adjustments of feed gas rates. Their point indications had the same limitations as the mass flowmeter indications, and were of limited usefulness in two other ways. The ball flows gave very non-linear flows and did not give simple factors to convert for different gas compositions. The meters were frequently fouled or "sticky" from chlorine corrosion products or solids entrained in the exit gases.

C.2 Product Gas Reactors and Traps

Reaction and removal of individual components of the product gases by fixed beds of solids was the basis for all three types of material balances. The weight changes of the fixed beds showed the amounts of material reacted. The removal of individual components resulted in flow differences that were a measure of the amount and also allowed use of CO_2 and CO concentration measurements. The reactors were designed to minimize the total weights in order to give weight material balances to 0.1- or 0.01-g precision using laboratory balances. Attempts to use liquid scrubbers for the initial tests[3] were troublesome and unsatisfactory.

The Cl_2 leaving the quartz reactor was trapped by copper foil in a Pyrex tube inside a furnace at 375 to 435°C. The reaction was visible as a sharp interface with plug flow, but the products at higher Cl_2 rates collected as solidified melt on the bottom wall of the tube.

The CO_2 in the gas leaving the copper foil trap was collected by Ascarite II (8 to 20 mesh) in standard laboratory Drierite reactor units at ambient temperature. The reaction was observed to show a sharp interface by appearance and by heat generation. At high CO_2 rates, the Ascarite II became hot at the reaction interface and tended to soften and cake with high resistance to gas flow. This plugging was only a minor problem for the 4-cm chlorination reactor but resulted in serious flow interruptions for the 68-mm reactor. A 9.5-cm ID Ascarite absorber was then used without further difficulty.

The CO was oxidized to CO_2 using a packed bed of CuO wires in a Pyrex tube in a furnace at 425 to 480°C. This reactor gave a sharp reaction interface by appearance and no problems. The CO_2 from oxidation of CO was absorbed with a similar reactor and results as for the CO_2 leaving the copper foil trap for Cl_2.

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