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COMPARISON OF PHOSGENE, CHLORINE, AND HYDROGEN CHLORIDE AS REAGENTS FOR CONVERTING MOLTEN $CaO.CaCl_2$ TO $CaCl_2$

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One method at Los Alamos for preparing impure plutonium metal from the impure oxide is by batch reduction with calcium metal at 850°C in a $CaCl_2$ solvent. The solvent salt from this reduction is currently discarded as low-level radioactive waste only because it is saturated with the CaO byproduct. We have demonstrated a pyrochemical technique for converting the CaO to $CaCl_2$ thereby incorporating solvent recycle into the batch reduction process. We will discuss the effectiveness of HCl, Cl_2, and $COCl_2$ as chlorinating agents and present initial data on regenerating and recycling actual spent process solvent salts.

Introduction

Impure plutonium metal is produced by the pyrochemical reduction of impure plutonium dioxide using molten calcium metal in a liquid calcium chloride solvent (1).

$$PuO_2 + 2Ca^\circ \xrightarrow[850^\circ]{11CaCl_2} Pu^\circ + 2CaO.11CaCl_2 \qquad (1)$$

This direct oxide reduction process (DOR) is a batch operation where the solvent salt performs a variety of functions during the reaction: it acts as a heat sink during the exothermic reduction of PuO_2, it provides a medium to control the reaction, and it dissolves the CaO byproduct to 18 mol% (10 wt%) which permits good plutonium metal coalescence after the reduction is complete.

Because of the limited solubility of CaO in $CaCl_2$, the solvent salts are discarded as low-level radioactive waste after each reduction. There are numerous advantages (2) for developing a procedure to regenerate the spent salts; briefly they include

- reduction of process waste from DOR
- improvement in overall process yields
- potential for producing a pure solvent salt
- potential for producing a pure plutonium product from pure reagents
- potential for optimizing the DOR process
- potential for oxidizing excess calcium metal to meet WIPP disposal criteria

We have initiated a program to define a process that addresses each of the advantages listed above and also determined the feasibility of DOR salt regeneration and recycle. This summary details our experience in salt recycle, both from radioactively hot and cold viewpoints.

In theory, the regeneration of spent DOR salts could be accomplished through any of three approaches: the electrolytic reduction of CaO and subsequent recovery of the calcium metal (3), precipitation of CaO, or by the chemical conversion of CaO to $CaCl_2$ using an appropriate chlorinating agent. Preliminary work at Argonne National Laboratory investigating the electrolytic reduction of CaO was promising, but it was felt too much time was required for proper cell design and development. Precipitation studies were also unsuccessful because of poor phase separation and incomplete CaO solute removal from the $CaCl_2$ solvent. The final approach, CaO conversion to $CaCl_2$ by chlorination, however, appeared very promising from initial small scale experiments.

This initial success encouraged us to scale the system to near full scale (3-5 kg spent salt) and to begin a program investigating the parameters necessary for spent salt recycle.

Because of our long-range goal to convert DOR from a purely batch to a semi-continuous operation by regenerating and recycling spent salts, we felt it necessary to accomplish regeneration of a 5 Kg salt in approximately two hours. This would provide the basis for further process development.

The success of this recycle program depends on maintaining or improving salt quality during regeneration. Plutonium is a very active metal solvent and trends to strip metal impurities from salt (Table I). This is the principle reason the DOR process has not been able to produce a "pure" metal (> 99.9%) from "pure" reagents. If we can regenerate a salt while maintaining or improving its quality, then pure metal production from this process is more feasible. We have selected three major analytical determinations to help evaluate the final salt: it will be necessary to maximize CaO rechlorination, to minimize residual oxides present in the salt (oxygen is a calcium consumer in DOR), and to minimize or eliminate the introduction of metallic impurities into the salt.

Regeneration Procedure

All research and process development was conducted in radioactively cold settings using synthetic spent DOR salt ($CaCl_2$.10 Wt% CaO.1 Wt% Ca°). We did not make any attempt to simulate the trace plutonium metal that would be present in the actual salts.

TABLE I. ESTIMATES OF ELEMENT SOLUBILITIES IN PLUTONIUM AT 800°C (4)

Element	Atom %	Wt%	Element	Atom %	Wt%
Silver	6.5	2.6	Nickel	45.0	16.7
Aluminum	10.0	1.2	Lead	14.0	12.4
Gold	7.0	5.8	Platnium	9.0	4.2
Beryllium	7.0	0.3	Rhenium	2.4	1.8
Bismuth	8.5	7.5	Rhodium	19.0	9.2
Carbon	2.3	0.1	Silicon	7.5	0.9
Cadmium	1.0	0.5	Tin	0.9	0.4
Cobalt	38.0	13.1	Tantalum	0.2	0.1
Chromium	3.3	0.7	Titanium	22.5	5.5
Copper	52.0	22.4	Thulium	4.1	2.9
Iron	27.0	8.0	Vanadium	1.5	0.3
Gallium	23.0	8.0	Tungsten	0.01	0.01
Hafnium	11	8.4	Yttrium	16.0	6.6
Magnesium	22.5	2.9	Zinc	30.0	10.5
Manganse	30.8	9.3	Zirconium	5.4	2.1
Molybdenum	2.8	1.1			
Niobium	1.5	0.6			

The method used in all experimentation was to place the 3.0 kg salt in a 15-cm-OD by 38-cm-tall vitrified magnesia crucible that was nested in a stainless steel containment can inside a stainless steel furnace tube (Fig. 1). After placing an argon atmosphere above the salt, the apparatus was resistance heated to 850°C using a Lindberg Model 6015S furnace. The melt was sparged with a chlorinating agent (HCl, Cl_2 or $COCl_2$) for a fixed time at a fixed flowrate. Samples were withdrawn from the melt initially and at selected intervals during the regeneration cycle to determine CaO conversion profiles and residual oxygen profiles as functions of gas contact time. After chlorination, the system was purged with argon and the salt cooled. All off-gas from the system was directed through a caustic scrubber system before venting to the atmosphere.

Results

It is possible to write several thermodynamically stable chemical reactions describing the stoichiometry of CaO, and calcium metal conversion to $CaCl_2$ using HCl, Cl_2, and $COCl_2$ (5,6). The kinetics of these reactions, however, are not understood nor do we

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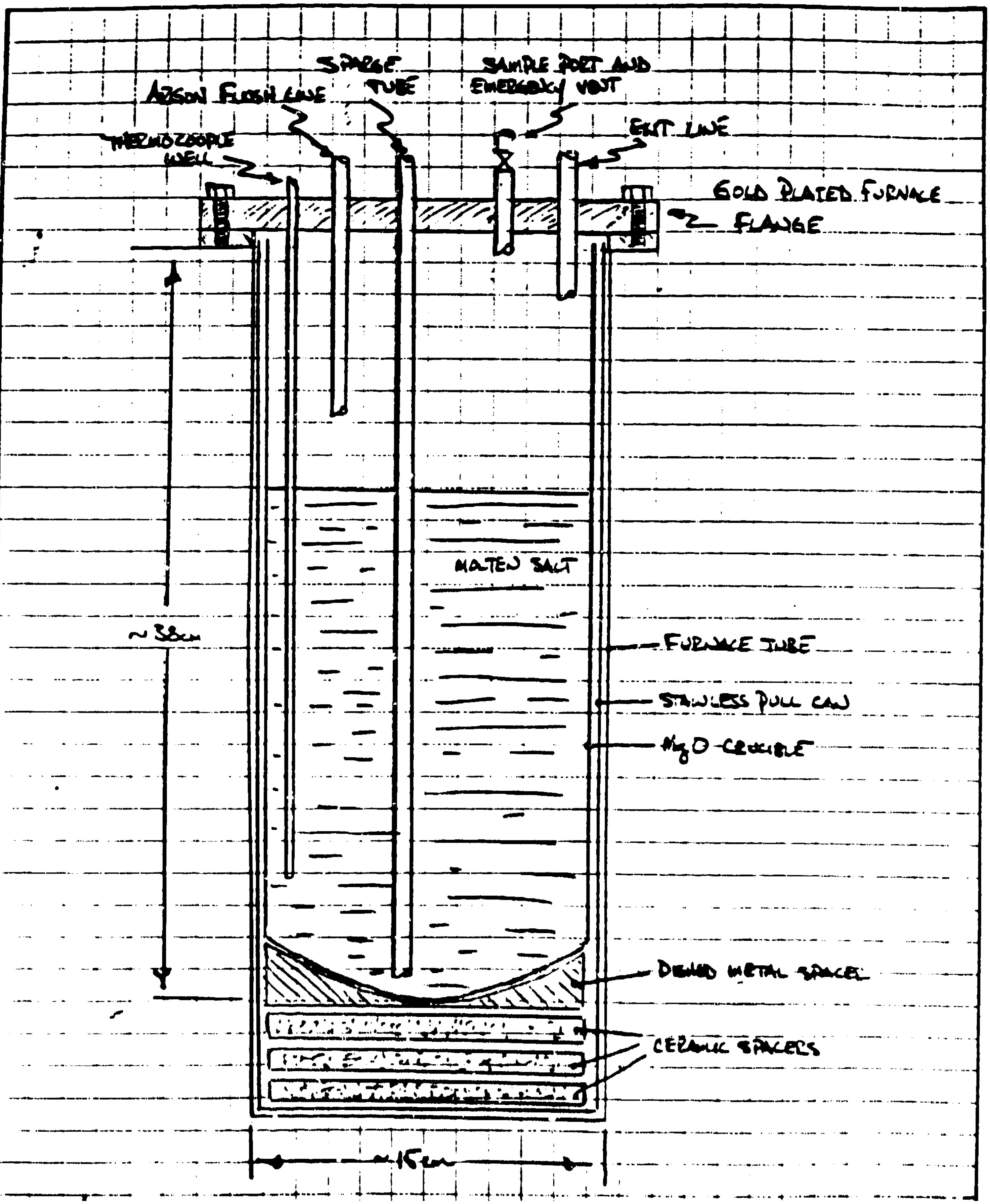

anticipate any future investigations into this area. For the three regenerant gases, general relationships can be written to help describe the reactions:

$$\mathrm{Ca + CaO + 4HCl \rightarrow 2CaCl_2 + H_2O + H_2} \qquad -136\ \mathrm{Kcal/molCaO} \qquad (2)$$
$$\mathrm{Ca + CaO + 3Cl_2 \rightarrow 3CaCl_2 + O_2} \qquad -\ 71\ \mathrm{Kcal/molCaO} \qquad (3)$$
$$\mathrm{Ca + CaO + 3Cl_2 \rightarrow 2CaCl_2 + Cl_2O} \qquad -154\ \mathrm{Kcal/molCaO} \qquad (4)$$
$$\mathrm{Ca + 4CaO + 6Cl_2 \rightarrow 5CaCl_2 + 2ClO_2} \qquad -\ 47\ \mathrm{Kcal/molCaO} \qquad (5)$$
$$\mathrm{Ca + CaO + 2COCl_2 \rightarrow 2CaCl_2 + CO_2 + CO} \qquad -249\ \mathrm{kcal/molCaO} \qquad (6)$$
$$\mathrm{Ca + 2CaO + 2COCl_2 \rightarrow 2CaCl_2 + CaCO_3 + CO} \qquad -211\ \mathrm{kcal/molCaO} \qquad (7)$$

Additional phosgene reactions can also be written that incorporate the oxy-chloro and oxygen products from the chlorine reactions.

Reageneration experiments with phosgene, chlorine, and anhydrous hydrogen chloride indicate that CaO alkalinity can be effectively reduced by any of the three reagents (Fig. 2). But since residual oxygen in final salt will react with calcium metal in the recycle step to form CaO, the residual oxygen profiles shown in Fig. 3 are a better indicator for regeneration efficiency. These profiles illustrate the difficulty in removing residual oxygen from the system. Regeneration with chlorine results in the best performance followed by HCl and then $COCl_2$. Possible explanations for these results may be with the oxygenated byproducts from the potential reactions. In most cases, these byproducts have low boiling points (<100°C) so that their vapor pressures at 850°C would be very large. Their solubilities in molten $CaCl_2$, however, are unknown. This solubility or the possibility of secondary reaction may contribute to the slower oxygen removal rates exhibited by the HCl or $COCl_2$.

When considering $COCl_2$ as the regenerant, CO_2 and $CaCO_3$ are proposed byproducts in the conversion reactions. Originally, we felt the carbonate reaction was predominant because of the slow oxygen removal rate and also because of the carbonate profiles shown in Fig. 4. This figure shows the dependence of carbonate concentation (as determined by carbonate specific ion electrode) on the regenerant gas flowrate. We felt the carbonate concentations peaked during regeneration as a result of $CaCO_3$ formation and then decomposition (calcite decomposes ~900°C). It was only after x-ray diffraction analysis on the salt indicated the absence of $CaCO_3$ that we considered dissolved CO_2 as both the carbon and oxygen source illustrated in Fig. 3 and Fig. 4. Additional tests are being conducted to help verify this new assumption.

In either case, the presence of carbon in reagents is deterimental to the success of pyrochemical operation because of the ability to form plutonium carbide, a high melting alloy at relatively low carbon concentrations. This compound is extremely difficult to separate pyrochemically. The resulting stability of carbon and oxygen in phosgene-regenerated salts and also the extreme toxicity and corrosiveness of the reagent have encouraged us to

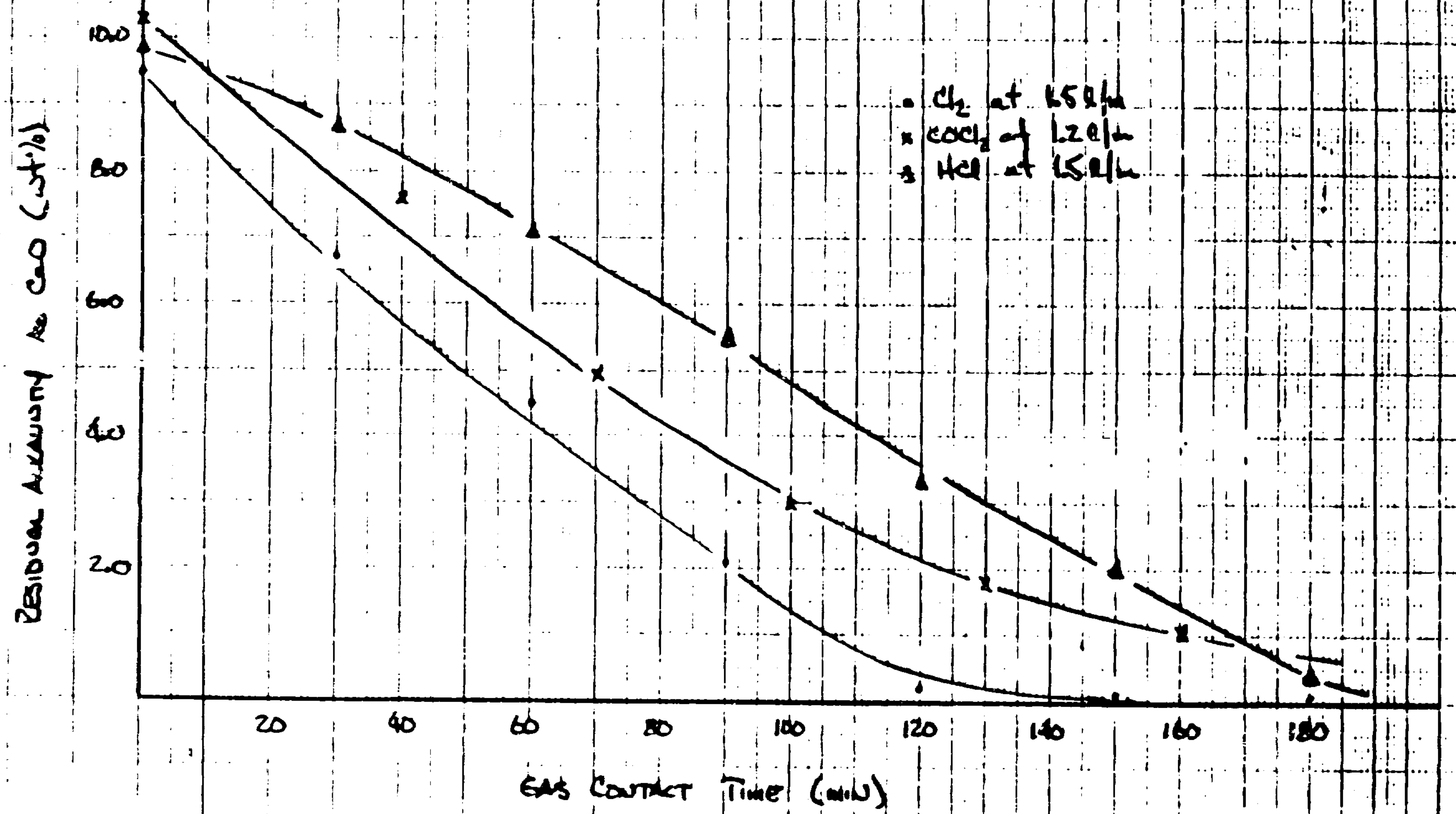

FIG. 2 RESIDUAL CALCIUM OXIDE IN REGENERATED SALTS

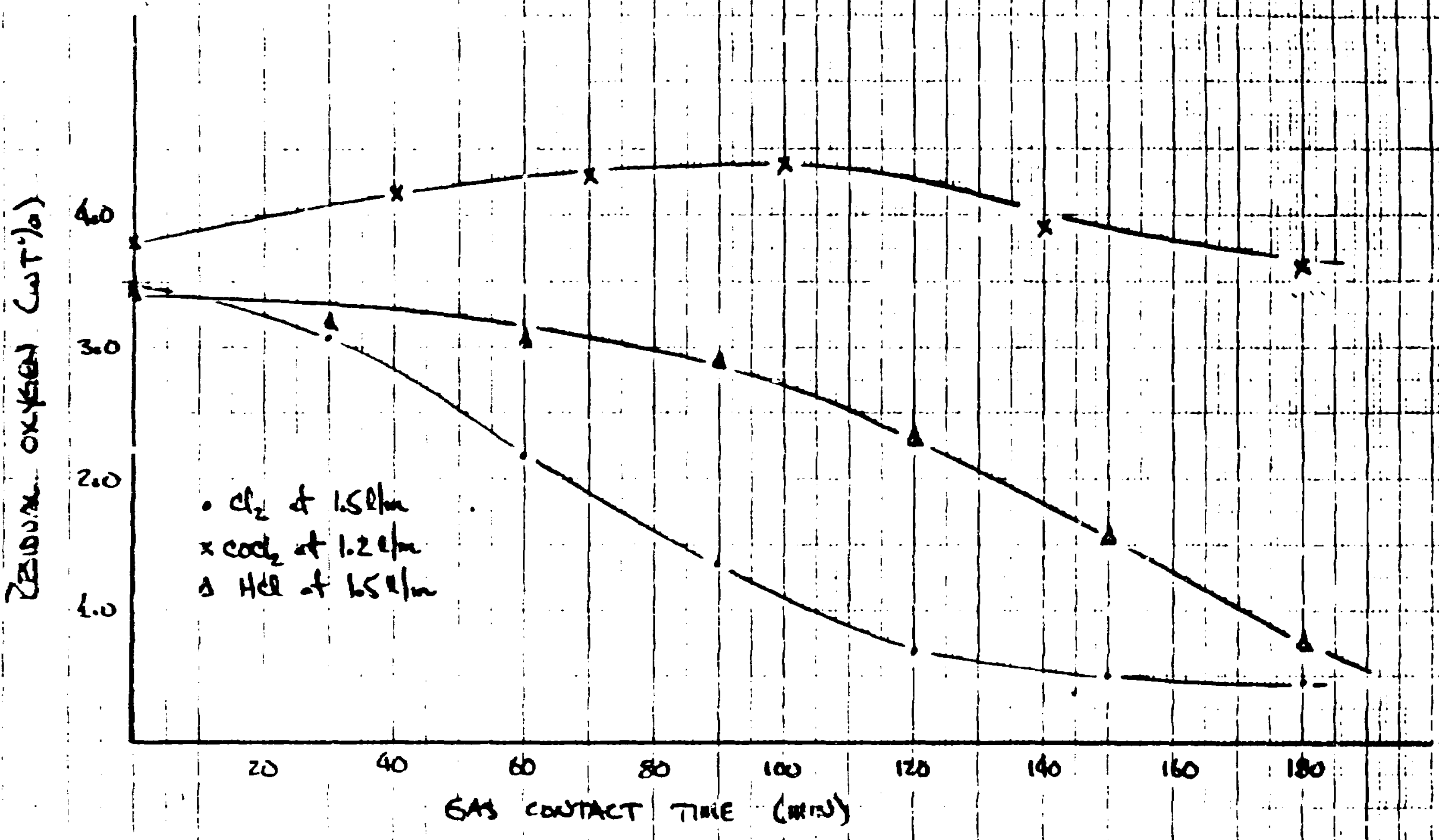

FIG 3. RESIDUAL OXYGEN IN REGENERATED SALTS

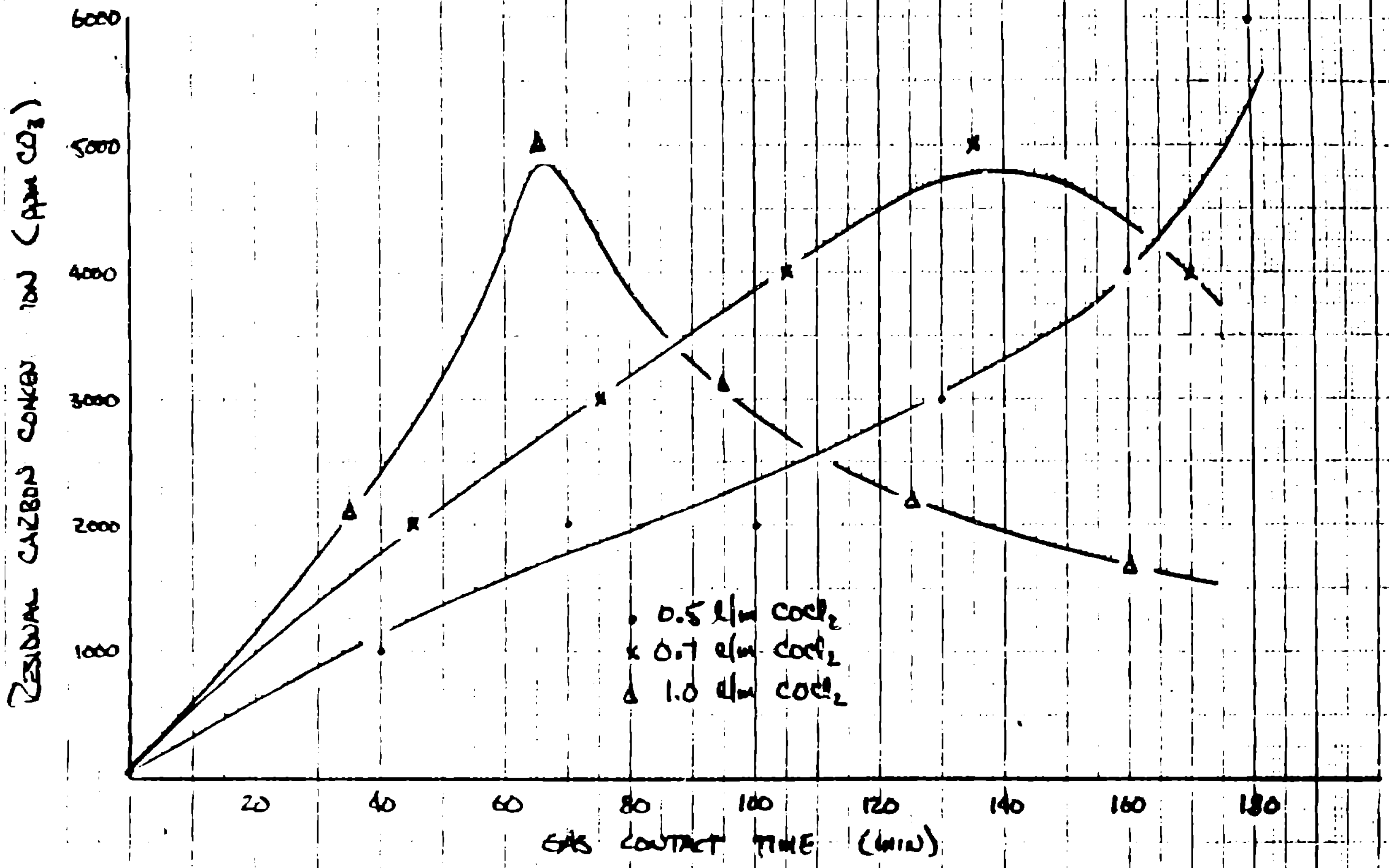

FIG 4 RESIDUAL CARBON (AS CO_3) IN REGENERATED SALTS AS A FUNCTION OF PHOSGENE FLOWRATE

eliminate phosgene as a candidate for DOR salt regeneration experiments. Hydrogen chloride and chloride, however, were evaluated further and are currently undergoing comparison in regenerating the actual spent DOR salts.

Because of the desire to rapidly regenerate the salt (∿5 kg, in ∿2 hr), we initiated an optimization program for HCl and Cl_2 to maximize regeneration and minimize residual oxygen. Since we felt constrained to use existing equipment (our reaction vessel configuration was therefore fixed), we concentrated on optimizing our gas/solution contact mechanism. Operating at high gas flowrates while minimizing solution splashing would give us efficient regeneration in the minimum time and with minimum salt loss. We are currently using an openend ceramic tube for gas introduction and have been able to effectively regenerate 5+ kg in 2 hours using chlorine at flowrates between 3-5 ℓ/min. Before deciding on openend tubing, we made several attempts at constructing suitable gas dispersion devices. Our high-porosity metal frits and perforated metal and ceramic tubes all suffered from mechanical failure or severe corrosion.

Figures 5 and 6 illustrate the effect of HCl flowrate on CaO conversion and residual oxygen during the course of typical regenerations. The trend of these curves is not surprising with an increase in flowrate resulting in quicker regeneration. Profiles using chlorine are similar, though its performance is much improved over HCl as was shown previously in Fig. 2.

Semi-qualitative metal analyses were performed on all of our regenerated salts to determine the extent of dissolution of wetted parts and other internal portions of the apparatus shown in Fig. 1. In all cases there was evidence of salt contamination by constituents of the apparatus. Figures 7 and 8 show the corrosive effects of HCl, Cl_2, and $COCl_2$ on the wetted ceramic parts. For the gas introductory tube we used alumina or vitrified magnesia, and the reaction vessel was always vitrified magnesia. Also in many cases we have seen high levels (500-1000 ppm) of stainless steel components present in the salt (Fe, Cr, Ni, Cu, Mn, etc). We feel this is due, in part, to the circulation of corrosive off-gas in the vapor space above the salt before it actually vents from the system.

We have been successful, however, in minimizing contamination from stainless steel by gold-plating the top furnace flange; by raising the magnesia reaction vessel as high in the furnace tube as possible; and by introducing an argon 'flush' line to the system to sweep the vapor space and force the off-gas out of the system as quickly as possible. The alumina contamination can be eliminated by changing to a magnesia sparge tube. The magnesia contamination, however, is inevitable but does not pose a major problem at this time. It reduces to magnesium during the recycle step by reacting

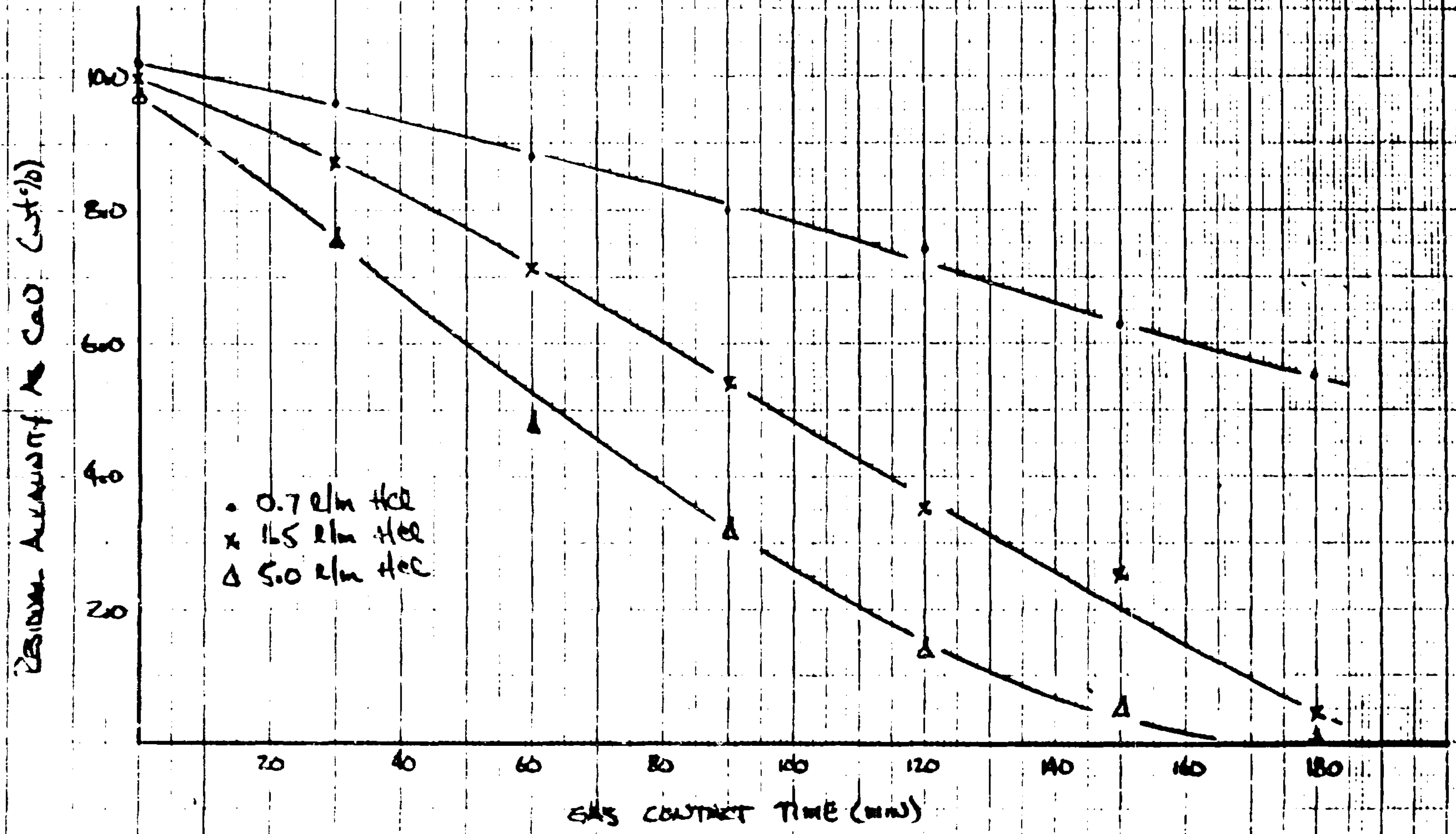

FIG. 5 RESIDUAL CALCIUM OXIDE IN REGENERATED SALTS AS A FUNCTION OF HCl FLOWRATE

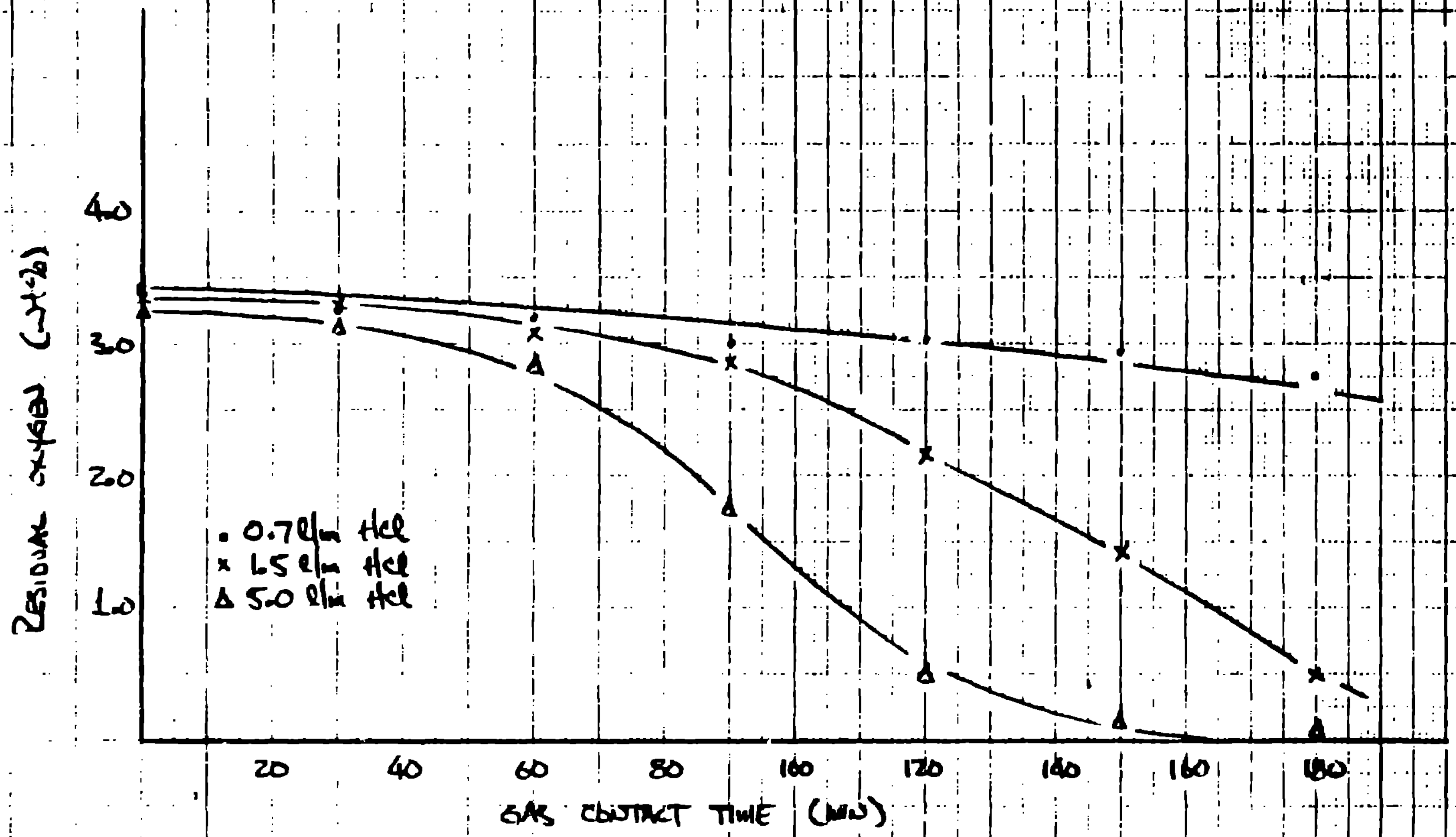

FIG. 6 RESIDUAL OXYGEN IN REGENERATED SALTS AS A FUNCTION OF HCl FLOWRATE

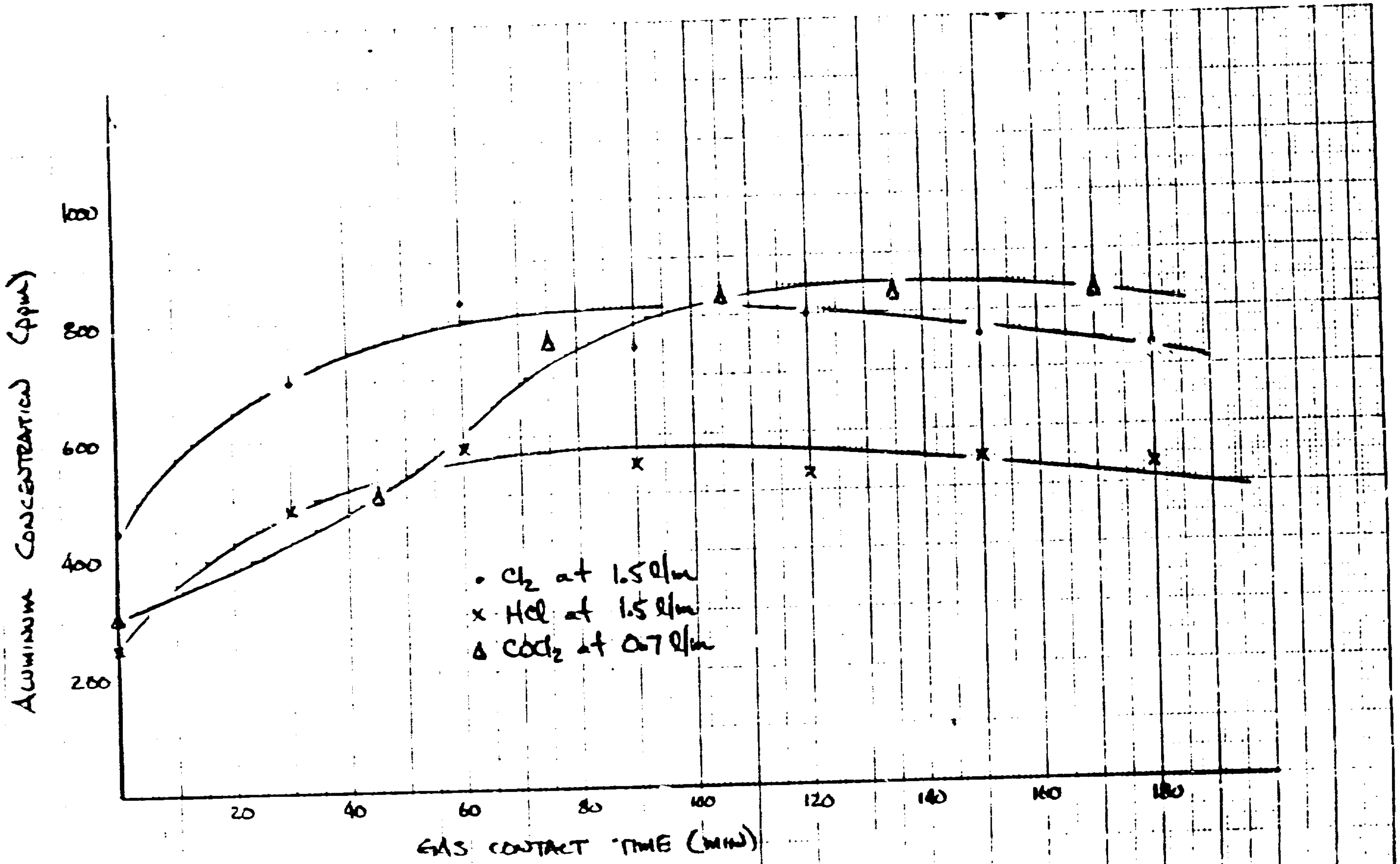

FIG. 7 ALUMINUM BUILDUP IN REGENERATED SALTS FROM DISSOLUTION OF ALUMINA HARDWARE

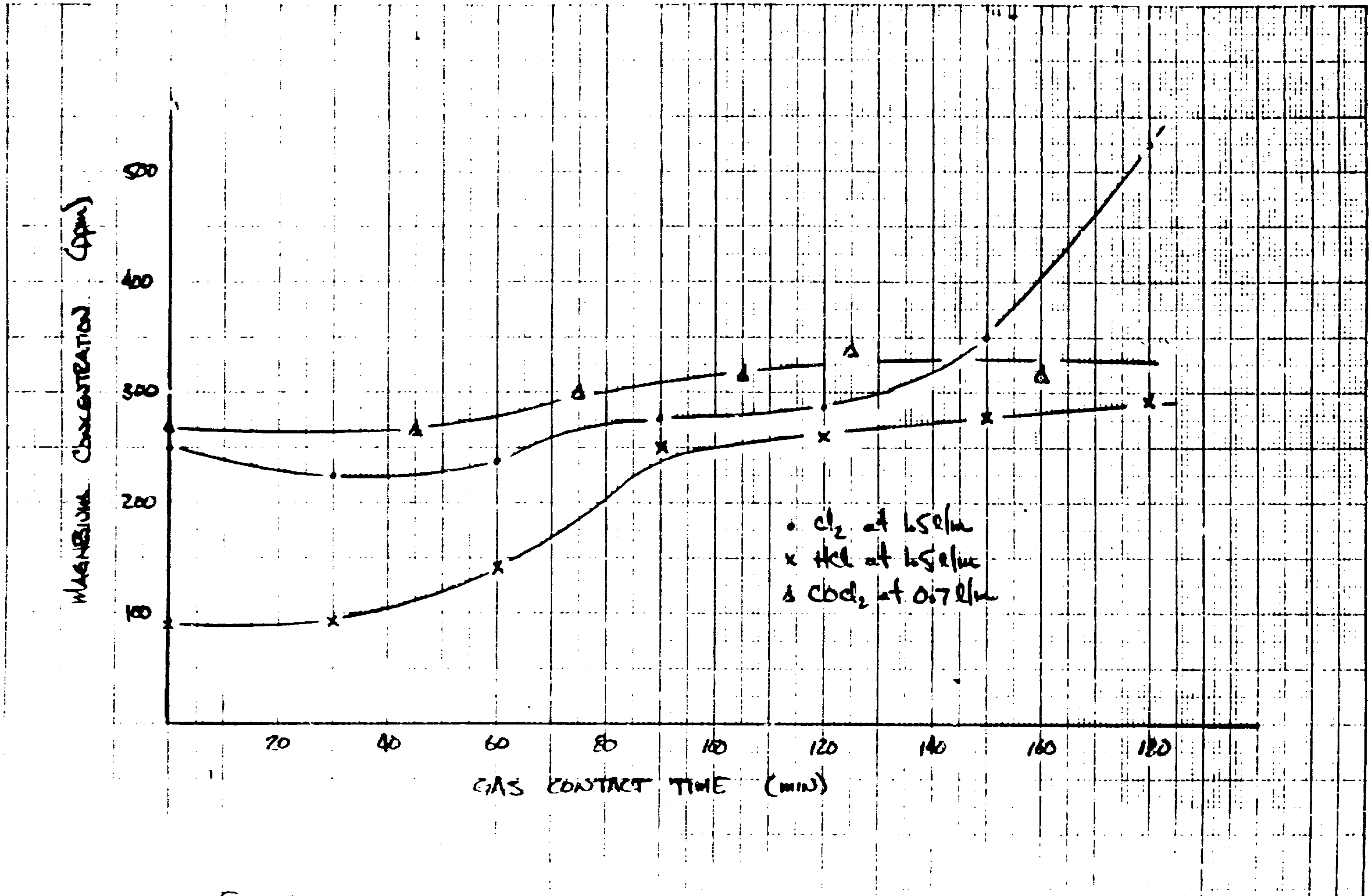

FIG. 8 MAGNESIUM CONCENTRATION IN REGENERATED SALTS FROM

with the calcium, volatilizing, and collecting in the cooler vapor space of the furnace tube.

Results of actual DOR Salt Regeneration and Recycle.

As a result of the development experiments using synthetic spent salts, we have adapted gloveboxes in our plutonium facility and are currently demonstrating DOR salt recycle on a full-scale batch basis. We regenerate a 5.0 to 5.5 kg salt in ∿2 hr with chlorine or HCl at flowrates between 3 and 5 ℓ/min. At these flowrates, both reagents effectively regenerate the salt. Chlorine, however, produces the better quality salt as indicated by its regeneration performance and subsequent recycle performance.

The presence of trace plutonium in the salts does not appear to effect regeneration in any way. The excess free calcium metal, however, does not behave as we expected. We felt the free calcium would react quickly with the regenerant gas and be converted to $CaCl_2$ early in the process. Our experience is that the buoyant calcium is effectively pushed to the wall of the reaction vessel by the gas bubbling through the salt. As this occurs, its ability to contact the chlorinating agent is severely reduced and it goes through the regeneration procedure partially intact. This is not a major problem; it only reduces the possibility of relying on this technique to fix or oxidize the calcium to meet WIPP criteria for multimate disposal.

Plutonium metal produced from the recycle step has proven to be of better quantity and quality than we originally expected. Metal yields from our recycle 5-kg have averaged slightly better than in production DOR (96% vs 94%). This is due in part to our using a consistent, high quality PuO_2 as opposed to production DOR using the lesser quality foundry grade PuO_2.

We are using the high quality feed to minimize variables in the process and allow us to better evaluate regeneration and recyle and also to evaluate the potential for pure metal production from pure reagents. Several DOR runs using this feed material have produced metal products whose plutonium content exceed 99%. Metal impurities are essentially the ones we previously discussed - stainless steel components and ceramic components. This product from DOR does not meet plutonium product specifications and will need further treatment. We are currently generating several kilograms of this metal to evaluate in subsequent processing steps.

Conclusions

o Regeneration of actual spent DOR salt can be effectively accomplished by either HCl or chlorine.

- **Based on synthetic spent salt regeneration experiments, phosgene was eliminated from further consideration as a regenerant gas because of carbon and oxygen stability in the product salt.**
- **We have demonstrated the ability to effectively regenerate 5+ kg of spent DOR salt in ∿2 hr using chlorine at flowrates of 3-5 ℓ/min.**
- Calcium metal appears to be incompletely converted to $CaCl_2$ during regeneration.
- Plutonium metal yields and metal quality using recycled salt are very comparable to results from production DOR.

Future Topics

For the short term (calendar 1985), we are planning our first series of tests into converting DOR from a purely batch system to a semi-continuous system. We will also continue with our materials compatibility studies and our modest equipment development program.

For the longer term, we expect to have determined the feasibility of our initial concepts regarding the evolution of DOR; we should have an answer to our materials compatibililty concerns; and will have determined if our equipment development program can support our DOR optimization goal.

Acknowledgement

Without the help of dedicated technicians who routinely performed and commented on these experiments, the development of this program would have suffered. For these reasons and more, we would like to thank A. E. Buckholz, W. J. Chavez, W. K. Drennan, D. W. Anderson, and J. Y. Coulter for their contributions in regenerating the synthetic spent salts; and also J. J. Simpson, and C. C. Davis for their contributions in regenerating and recycling the actual spent salts.

REFERENCES

1. L. J. Mullins, D. C. Christensen, and B. R. Babcock, "Fused Salt Processing of Impure Plutonium Dioxide to High-Purity Plutonium Metal", Los Alamos National Laboratory report LA-9154-MS, January 1982.

2. M. S. Coops and D. F. Bowersox, "Non-Aqueous Processing Methods", Los Alamos National Laboratory report LA-10169-MS, September 1984.

3. C. H. Bean and M. J. Steindler, "National Program for Pyrochemical and Dry Processing of Spent Reactor Fuels", in Actinide Separations, pp 177-189, J. D. Navratil and W. W. Schulz, ed., ACS Symposium Series, American Chemical Society (1980).

4. F. H. Ellinger, W. H. Minor, D. R. O'Boyle, and F. W. Schonfeld, "Construction of Plutonium Alloys", Los Alamos Scientific Laboratory report LA-3870, (1968).

5. R. C. Weast, ed. CRC Handbook of Chemistry and Physics, CRC Press, 65th Ed, ppg D52-D93.

6. K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy, XIII; High Temperature Heat Content, Heat Capacity, and Entropy Data for the Elements and Inorganic Compounds", USBM Bulletin 584, (1960).