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EUROPEAN ATOMIC ENERGY COMMUNITY - EURATOM

**HALIDE SLAGGING OF RARE EARTH
FISSION PRODUCTS IN MOLTEN URANIUM**

by

G. SENNEWALD, C. DAVID and J.G. WURM

1968



**Joint Nuclear Research Center
Ispra Establishment - Italy**

**Chemistry Department
High Temperature Chemical Technology**

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Printed by Guyot, s.a.
Brussels, November 1968

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Luxembourg, November 1968 - 36 Pages - 8 Figures - FB 50

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A decontamination factor of 3×10^4 for Ce and La has been reached under the following simulated conditions: 1 kg of irradiated U (10 % burnup) with 100 gr of UCl_3 in the slagging salt at 1,250 °C.

Two other results are mentioned :

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SUMMARY

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Two other results are mentioned:

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KEYWORDS

SEPARATION PROCESSES
FUSED SALTS
URANIUM CHLORIDES
URANIUM 235
CHLORINATION
CERIUM
LANTHANUM
URANIUM

DECONTAMINATION
SLAGS
CALCIUM CHLORIDES
BARIUM CHLORIDES
REACTION KINETICS
SOLUBILITY
LIQUID METALS
REPROCESSING

HALIDE SLAGGING OF RARE EARTH FISSION PRODUCTS IN MOLTEN URANIUM

1. INTRODUCTION (*)

Pyrochemical processes are developed for the treatment of fast breeder fuels in close coupled reactor processing facilities. Compared to the aqueous solvent processing the major economic incentives for the development of dry processes are: short cooling times, low fuel inventories, compact processing equipment, less criticality problems, no radiation damage to the chemicals used, and the production of solid radioactive waste. The low decontamination factors ($\approx 10^2$) which are obtained with pyrometallurgical processes are well acceptable for fast breeder fuels since remote refabrication of the fuel element will be almost necessary in any case. Even if the fission products are well separated from a short cooled fuel the remaining γ activity coming from the Pu isotopes is still too high for a fuel refabrication without shielding.

Pyrometallurgical reprocessing has been investigated as early as 1950 in England and the U.S.A. [1,2,3,4,5]. Perhaps, the best illustrative example in this field is given by the EBR II Fuel Cycle Facility at Idaho which has been abundantly described in the literature [6-17]. In this "oxide dropping" process the fuel consisting of an U-Mo alloy is melted in a ZrO_2 crucible. The volatile fission products are vaporized and the rare earth fission products are slagged at the crucible wall. The so-processed uranium alloy is transformed again into small pins for immediate use in the reactor. All operations are done remotely. This oxide dropping as simple as it looks, has however one major drawback. In the oxide skull which is composed of R.E. oxides sticking to the crucible wall, some trapped U-Pu fuel particles must be recovered.

This leads to a costly skull "reclamation process".

Recently, plans have been made by A.N.L. to replace the oxide dropping process at Idaho by the more sophisticated "Salt Transport process" [18]. This new liquid metal salt process is not only suitable for fission product removal but also for the Pu-U separation. Therefore the skull reclamation problems are eliminated and the process is operated at much lower temperatures. However, both Pu and U must be recovered from their liquid metal solvents by distillation. When the present work was started out in early 1964, the Salt Transport process was not yet known and at that time the purpose was to find an alternative to the oxide dropping process, without having the trouble with the skull reclamation.

(*) Manuscript received on August 14, 1968.

It was decided to perform the R.E. fission products separation from molten uranium metal with molten salts in an inert crucible.

It was decided also to perform this reaction above the melting point of uranium without the addition of other liquid metal solvents (like Zn, Bi,...) in order to simplify the refabrication procedure. Furthermore UCl_3 instead of $MgCl_2$ was chosen as the slagging reagent. It was obvious that at these temperatures a materials problem had to be faced, but on the other hand it was also clear that a good reaction kinetic could be expected for the R.E. slagging performance.

2. EXPERIMENTAL

2.1 Materials Preparation

2.1.1 The salt phase

For the halide slagging experiments of the uranium-rare earth alloys the choice of a salt phase is very restricted. First of all, the uranium melting point ($1134^{\circ}C$) imposes a working temperature of about $1200^{\circ}C$. Therefore the salt phase vapor pressure must be low enough to stand this temperature for several hours. This would discard iodides or bromides since they are either volatile or unstable, and also the fluorides because of their corrosive nature. Finally, the chlorides are the best choice. From the free energies of formation (see Glassner tables [19]) it can be seen that among the chlorides only UCl_3 and $MgCl_2$ are suitable chlorinating agents for the R.E. metals. For practical reasons only UCl_3 , dissolved in a $BaCl_2$ - $CaCl_2$ eutectic mixture, was considered in our experiments. Both solvent salts, $BaCl_2$ and $CaCl_2$, were prepared from their respective reagent grade hydrates $BaCl_2 \cdot 2H_2O$ and $CaCl_2 \cdot 6H_2O$ under the following conditions:

- Dehydration under a vacuum of 10^{-2} Torr at $100^{\circ}C$ for 5 hours
- Heating in a dry HCl atmosphere up to the melting point within 3 hours
- Bubbling of HCl-gas through the melt for another 5 hours.

Finally, the two purified salts were melted together in the eutectic proportion. The UCl_3 was prepared "in situ" in the solvent salt by means of a AgCl electrolysis. For this purpose the amount of 20 w/o AgCl (reagent grade) was added to the $BaCl_2$ - $CaCl_2$ solvent. The set-up of the electrolytic cell is described in fig. 1.

The graphite crucible cell is confined inside a quartz tube device under an inert atmosphere (purified argon). The cathode is composed of a liquid tin bath, in an Al_2O_3 crucible, located at the cell bottom. A pure uranium bar, immersed in the salt bath, acts as the anode. A thermocouple and a stirring device complete the equipment. The operating conditions were as follows:

- cell voltage : 500 mV
- current : 1 Amp.
- bath temperature : 700°C
- Faraday efficiency : 100%

All the AgCl was transformed into UCl_3 . No higher uranium chlorides could be detected by X ray-diffraction (20). The deposited silver dissolved completely in the liquid tin cathode. (The cell was dimensioned for 500 gr salt charges.)

2.1.2 Preparation of the uranium rare earth alloys

The R.E. metals came from Leytess Metal Corp. with a guaranteed purity of 99,99%. The main impurity, tantalum, was of no concern for our experiments. The uranium metal came from Nukem (Germany) with 50 ppm of Ca as the main impurity.

The BeO crucible which is normally used for the halide slagging, is unfortunately not suitable for the alloy preparation. Cerium reacts with BeO forming an interceramic compound of the Me BeO_4 type. This side reaction does not take place once the cerium is dissolved in the uranium, at low concentrations. Therefore, the halide slagging is still possible in BeO crucibles, but for the U-Ce alloy preparation a Ta crucible is to be preferred. According to the Ta-U phase diagram given by Schramm [21] Ta dissolves in liquid U up to 1 wt% limit at 1140°C . (The two metals form a solid solution at 1175°C covering the concentration range from 2-98%.)

Therefore, it was expected that Ta would resist in contact with liquid uranium up to 1170°C . In fig.2 are shown three Ta crucibles after a 30 minutes contact time at 1140°C , 1160°C and 1180°C . Only at 1140°C the crucible was not attacked. The tantalum crucible was made from 0.5 mm Ta sheet and argon welded. Prior to the alloy preparation the R.E. metal

was neutron irradiated in the Ispra-I reactor for gamma spectroscopy analytic purposes. The alloys were prepared in the vacuum furnace shown in fig. 4 which is described in details in the following chapter. Because of the great density difference and also because of the very small mutual solubility (22), the R.E. metal is floating on the surface of the liquid uranium. Therefore, stirring becomes necessary if the alloy is to become homogeneous (stirring 20-30 min. at 1140°C with 180 R.P.M.). After solidification the alloy adheres to the crucible and its extraction is very difficult. This is done in the following way: the tantalum crucible is placed in up-side down position upon a BeO crucible, the alloy is melted and flows into the BeO crucible. Then the ingot is cut into pieces and samples are taken for analysis.

2.2 The chloride slagging experiments: description of the equipment

For all the chloride slagging experiments of the U-RE metal alloys only pure BeO crucibles have been used. According to Rosen et al. [9] this container material is well suited for molten uranium. The BeO crucibles of "Berycer" type came from C.G.E. (France). The experimental cell is shown in fig. 3. It consists of a 100 mm quartz tube enclosure connected to a high vacuum pumping system (primary pump of 25 m³/h and 600 l/sec diffusion pump). The BeO crucible stands on a graphite disk which in turn is supported by another quartz tube. A Pt-Pt/Rh thermocouple touches the bottom of the BeO crucible. The graphite tube susceptor which surrounds the BeO crucible is heated by a 25 Kw, 500 MHz, H.F. generator (Philips). The top of the large quartz tube is closed by a water cooled aluminium head which is equipped with a sampling device as well as with vacuum tight passages for a stirrer and a second thermocouple. This latter one is shielded by a BeO tube. The sampling device consists of four sampling tubes (Ø 3mm) which can be moved vertically and to some extent also horizontally (fig. 3).

At the beginning the BeO crucible is filled with weighed amounts of metal and salt. Then it is held under a vacuum of 10⁻⁶ Torr for at least 12 h at room temperature. Then still under vacuum the temperature is raised stepwise during 5 h until the salt is molten which is at about 610°C for the BaCl₂-CaCl₂ eutectic mixture. Finally, the apparatus is filled with purified argon at 700 Torr and the temperature is raised to 1200°C. At this time the thermocouple is withdrawn from the crucible and the tantalum stirrer is introduced into the liquid metal and the salt. A stirring time of 30' at 150 R.P.M. will

be adequate to reach equilibrium. After a 3h sedimentation time samples are taken from each phase. For that purpose the argon pressure is raised to the atmosphere pressure. The sampling tubes are filled either with salt or metal by depression. They are withdrawn from the molten bath under depression until the samples are solidified.

The sampling operation must be done with great care to avoid mixing of the salt and metal phases. This operation can be repeated every 30' or 60'. In some cases only metallic samples are taken at four time intervals.

2.3 The preparation of the samples for analytic purposes

After the halide slagging experiment, the remaining metal, the salt and the already taken samples are analyzed in order to determine their relative contents of the R.E. metals.

The analyses are made by gamma counting of aqueous sample solutions.

3. RESULTS AND DISCUSSION

3.1 The equilibrium between cerium and eutectic mixtures of BaCl₂+CaCl₂

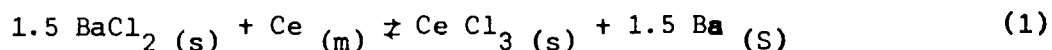
In one series of experiments Ce metal was equilibrated with the eutectic mixture of 63/35 mol % CaCl₂/BaCl₂ at temperatures between 1000 and 1500°K. In fig. 4 the obtained equilibrium concentration of Ce in the salt phase is plotted against the reversed value of the absolute temperature, which represents actually the Ce equilibrium concentration as an exponential function of the temperature.

In the solidified salt the X ray diffraction lines of metallic cerium have been identified. Therefore the transfer mechanism of Ce from the molten alloy to the salt phase can be explained either by a chemical reaction between Ce and the salt phase or a single metallic dissolution.

In order to clarify this point, the simpler reaction between Ce and BaCl₂ at 1473°K has been investigated in some more detail.

3.1.1 The reaction between Ce and BaCl₂ at 1473°K

The following equilibrium reaction between Ce and BaCl₂ was taken into consideration:



S designates the salt phase and m the metal phase.

The equilibrium constant of this reaction can be written as:

$$K = \frac{(\text{CeCl}_3^s) \cdot (\text{Ba}^s)^{1.5}}{(\text{BaCl}_2^s)^{1.5} \cdot (\text{Ce}^m)} \quad (2)$$

The expressions in parentheses designate the activities of the concerned components in their respective phases. Since the metal phase consists of pure Ce and the salt phase of pure BaCl₂, their activities can be taken as unity. Thus (2) becomes:

$$K = (\text{CeCl}_3^s) \cdot (\text{Ba}^s)^{1.5} \quad (3)$$

$$K = C_{\text{CeCl}_3^s} \cdot C_{\text{Ba}^s}^{1.5} \cdot f_{\text{CeCl}_3^s} \cdot f_{\text{Ba}^s}^{1.5} \quad (4)$$

where C and f are molar concentrations and activity coefficients respectively. From the stoichiometry of (1) we have the relation:

$$1.5 C_{\text{CeCl}_3^s} = C_{\text{Ba}^s} \quad (5)$$

This equation is correct only if it is assumed that all the Ba formed is dissolved in the salt phase and that there exists only a negligibly small distribution of Ba between the salt and metal phase. Since in these experiments the ratio $\frac{\text{salt}}{\text{metal}} = \frac{100}{1}$, the distribution of Ba between both phases can be neglected. The activity coefficient $f_{\text{CeCl}_3^s}$ can be estimated from the E.M.F.

in the three binary systems CaCl₂ - CeCl₃; KCl - CeCl₃; NaCl - CeCl₃ at 1.123°K. (see Senderoff et al. [23]). These authors compare the charge density of the metal ions, which is proportional to the quotient of the ionic valence and the third power of the crystal radius.

These authors have considered the charge density $\frac{z}{p^3}$ of the ions K⁺, Na⁺, Ca⁺⁺ and the measured activity coefficients of the Ce⁺⁺⁺ ion in the above systems. They have observed that these ions can be classified in the same order either by their $\frac{z}{p^3}$ values, or by the Ce⁺⁺⁺ activity coefficient.

In this classification the Ba⁺⁺ ion falls in between the K⁺ and Na⁺ ions. Therefore it is assumed that the deviation from ideality of the BaCl₂-CeCl₃ system is located in between the one of KCl-CeCl₃ and NaCl-CeCl₃ systems [23].

As a result, an approximative value of the E.M.F. difference between pure BaCl₂ and a mixture of BaCl₂ with 1 (mol %) CeCl₃ at 1123°K is obtained:

$$\Delta E = - 0.150 \text{ (volt)} \quad (6)$$

At hand of this value it is possible to calculate the activity coefficient of CeCl_3 for this same concentration at 1473°K

$$f_{\text{CeCl}_3^s} = 1.7 \cdot 10^{-2} \quad (7)$$

The equilibrium constant K at 1473°K is thus calculated using the extrapolated values of the standard free energy of formation of the Glassner table [19]

$$K = 1.66 \cdot 10^{-8} \quad (8)$$

Therefore:

$$C_{\text{CeCl}_3^s} = \frac{0,12 \cdot 10^{-3}}{f_{\text{Ba}^s} \cdot 0.6} \quad (9)$$

Equation (9) thus establishes the equilibrium concentration of CeCl_3 in the salt phase as a function of the activity coefficient of Ba in the salt phase.

In the following table some corresponding values of CeCl_3^s and f_{Ba^s} are combined:

f_{Ba^s}	10^{-3}	10^{-2}	10^{-1}	1	10	10^2	10^3	10^4
$\frac{C_{\text{CeCl}_3^s}}{0,12}$	$10^{-1.2}$	$10^{-1.8}$	$10^{-2.4}$	10^{-3}	$10^{-3.6}$	$10^{-4.2}$	$10^{-4.8}$	$10^{-5.4}$

Taking into account that f_{Ba^s} most probably does not assume other values than

$$10^{-3} \ll f_{\text{Ba}^s} \ll 10^3$$

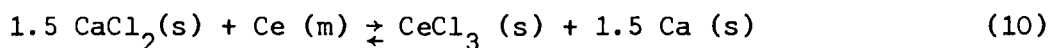
(this is assumed in analogy to the results obtained by the system Na-NaCl by Piontelli [24]), it is deduced that the theoretically possible values of $C_{\text{CeCl}_3^s}$ are included in the range

$$0,12 \cdot 10^{-1,2} < C_{\text{CeCl}_3}(\text{s}) < 0,12 \cdot 10^{-4,8}$$

On the basis of this approximative examination it is stated that in the most unfavorable case it exists a difference of two orders of magnitude between the experimentally observed equilibrium concentrations and the theoretical one. This difference is not great enough to disconsider the reaction (1) as a reasonable explanation of the observed Ce metal concentration in the salt phase.

3.1.2 The reaction between Ce and CaCl₂ at 1473°K

In the case of a reaction between Ce and CaCl₂ only a pure CaCl₂ salt phase is considered.



The reaction (10) at 1473°K leads to an equilibrium concentration of CeCl₃ in the salt phase which itself is dependant on the value of the activity coefficient $f_{\text{Ca}}(\text{s})$ in a similar way as reaction (1):

$$C_{\text{CeCl}_3}(\text{s}) = \frac{0,687 \cdot 10^{-3}}{f_{\text{Ce}}(\text{s})^{0.6}} \quad (11)$$

A comparison of equation (11) with equation (9) shows immediately the similarity of both expressions so that the same qualitative considerations are valid here. The reaction (10) could therefore be responsible for the experimentally observed Ce concentration of the salt phase.

3.1.3 Discussion

As the activity coefficient of the alkaline earth metals Ba and Ca in their respective chlorides are not available, the existence of the reactions (1) and (10) does not answer completely the question of the transfer mechanism of Ce from the molten metal to the salt phase.

A chemical reaction at the interface with a successive dissolution of the reagents in the salt phase is thermodynamically possible. Therefore a metallic dissolution of Ce in the salt phase cannot be excluded as a transfer mechanism since a dissolution of metals in foreign salts in the range of $\ll 1.0 \text{ mol } \%$ is well established in the literature [25 and 26].

TABLE 1

Coefficient K_D of La between liquid uranium metal and barium chloride

Temperature	Introduced quantities				Equilibrium concentrations		Distribution coefficient	Decontamination factor
	Salt	U	La (U)	$La^U_a \cdot 10^2$	$La^U_e \cdot 10^5$	$La^S_e \cdot 10^2$	$K_D = La^S_e / La^U_e$	$F = La^U_a / La^U_e$
(°C)	(g)	(g)	(mg)	(mol %)	(mol %)	(mol %)	-	-
1150	92,35	78,23	18,0	3,80	1,42	2,57	1820	2065
1170	94,05	84,50	15,0	3,11	1,52	1,99	1309	2064
1180	100,15	108,52	14,0	2,20	65,0	0,86	13,3	34 ⁺
1220	85,07	88,22	37,0	7,30	8,27	6,58	795	936
1250	80,30	94,75	11,0	1,94	10,30	2,50	244	189

⁺ In this experiment the equilibrium was not obtained.

TABLE 2

Coefficient K_D of the Ce between liquid uranium metal and barium chloride

Temperature °C	Introduced Quantities				Equilibrium Concentration		Distribution coefficient	Decontamination factor
	Salt g	U g	Ce(U) mg	Ce _a ^U mol %	Ce _e ^U · 10 ² mol %	Ce _e ^S mol %	$K_D = Ce_e^S / Ce_e^U$	$F = Ce_a^U / Ce_e^U$
1140	63,0	54,4	326	1,015	0,124	0,8673	702	822
1180	93,8	112,1	445	0,673	0,1314	0,5376	179	132
1200	80,3	94,8	376	0,673	2,718	0,7495	47	25
1220	96,7	111,9	985	1,497	1,168	1,520	130	128
1450	88,5	89,2	393	0,750	0,3429	0,995	290	219

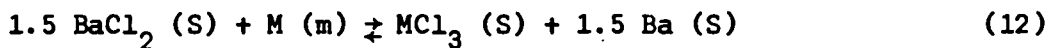
The hypothesis of a metallic dissolution seems to be supported by the presence of the Ce diffraction lines in the Debye-Scherrer pattern in the salt. It is, however, not certain whether in the liquid salt the Ce will also be present as a metal, and it is possible that the reactions (eq. 1) and (eq.10) in the liquid state primarily form $CeCl_3$ which on solidification is reduced to metal according to the great variations of the activity coefficients f_{BaS} and f_{CaS} . An analogous phenomenon has been observed by Fiorani [27] who analyzed the Cd-Cd Cl_2 system. Some evidence was found for a subchloride formation in the liquid salt phase, and metallic cadmium was present in the frozen solid salt phase.

3.2 The distribution of Ce and La between U and Ba Cl_2

The distribution of Ce and La between U and $BaCl_2$ has been measured as a function of temperature. The results are presented in tables 1 and 2. Fig. 5 and 6 give a plot of the distribution coefficients versus the inverse of the absolute temperature. The R.E. metal content of each phase was measured by gamma spectroscopy. The initial concentration of Ce in U was about 1,0 (mol %) and that of La in U about 10^{-2} (mol %). Although these concentration ranges differ by a factor of 100, the distribution coefficient vs. temperature plots for both R.E. metals are quite similar: the distribution coefficients decrease with increasing temperature.

3.2.1 The reaction between the R.E. metal and U alloys and $BaCl_2$

The following reaction is considered at $1473^\circ K$



its equilibrium constant K is:

$$k = \frac{(MCl_3^S) (Ba^S)^{1.5}}{(BaCl_2^S)^{1.5} \cdot (M^m)} \quad (13)$$

M = R.E. metals

Equation (12) and (13) are identical with equation (1) and (2), however the phases m and S are different in both cases:

m = alloy of R.E. metal and uranium

S = pure $BaCl_2$

Therefore, the activity of BaCl_2 in the salt phase is unity and the equation (13) is simplified:

$$k = \frac{C_{\text{MCl}_3}^{\text{S}} \cdot C_{(\text{BaS})}^{1.5} \cdot f_{\text{MCl}_3} \cdot f_{(\text{BaS})}^{1.5}}{C_{\text{M}}^{\text{m}} \cdot f_{\text{M}}^{\text{m}}} \quad (14)$$

The activity coefficients f_{BaS} and f_{Mm} are unknown and their evaluation is difficult because of lacking literature data. A quantitative examination of the equilibrium reaction (12) is therefore not possible.

The previous examination of reaction (1), however, has shown that its equilibrium may lead to the observed Ce concentration of the salt phase so that the same qualitative statement may be considered valid for reaction (12).

3.2.2 The solubility of Ce in liquid U

If we compare the Ce concentration between the system pure Ce metal - $\text{BaCl}_2/\text{CaCl}_2$ salt mixture and the system Ce - U alloy - pure BaCl_2 , nearly equal Ce concentration values in both cases are observed (1,6 mol % in the first case, 1,52 mol % in the second case at 1220°C). Since the first case value correspond to the solubility limit of Ce in the salt phase, it is assumed that the solubility limit of Ce in the salt phase was also attained in the second case.

Furthermore, in the case of the Ce distribution between U and BaCl_2 there was enough Ce available to attain the solubility limit concentration of Ce in the salt phase, the observed Ce concentration in the U metal phase necessarily corresponds also to its solubility limit.

Thus the values of the Ce concentration, given in table 2, indicate this solubility limit ($10^{-3} - 10^{-2}$ mol % between 1150° and 1450°C). We conclude therefore that in our U-Ce alloy preparation the Ce was only partially dissolved, while its major part remained in suspension by forced convection.

If we compare our Ce solubility measurements in liquid uranium (table 3) with those obtained by Haefling and Daane [22], there exists a difference of a factor 100.

TABLE 3

The solubility of Ce in molten U at different temperatures by Haefling [22] and our own data

Haefling		Own Data	
Temperatures °C	Solubility mol %	Temperatures °C	Solubility mol %
1150	1,995	1140	0.00124
1175	2,150	1180	0.00131
1200	1,937	1220	0.0168
1225	1,686	1450	0.00343
1250	2,522		

In a similar situation Tomlinson et al. [28] have investigated the solubility of Mg and Ca in their respective chloride. They found that after intensive stirring the two phases did not separate by simple sedimentation. They explained that the phenomenon of mutual suspensions in the two phases is the result of interfacial tensions between liquid salt-metal systems and liquid metal-metal systems. Therefore, it is very likely that this phenomenon is also predominant between U and R.E. metal alloys. In our own experiments we could find evidence of microsuspensions of the counterphase in almost all of the experimental samples. We conclude therefore that the solubility limits for Ce in U given by Haefling are too high and might be due to sampling errors.

3.2.3 The solubility of La in molten U

The preparation of a U-La alloy was even more difficult than the one of U-Ce. The maxim. La concentration in U which could be obtained was in the order of 10^{-2} mol %. The solubility limits of La in molten U as given by Haefling [22] are in the same order of magnitude as for Ce. Again we consider these values too high by a factor of 100, as evident from table 4 and for the same reasons as stated before.

TABLE 4

The solubility of La in molten U by Haefling and our own data

Haefling Data		Own Data	
Temperatures °C	Solubility mol %	Temperatures °C	Solubility mol %
1150	1,313	1150	0,038
1175	1,296	1170	0,0311
1200	1,380	1220	0,0730
1225	1,431	1250	0,0194

3.3 The distribution of Ce between U and the Salt Phase containing UCl₃

The distribution of Ce between molten U and the eutectic mixture of 35/65 mol % BaCl₂/CaCl₂ has been determined at different UCl₃ concentrations, in the salt phase and at a temperature between 1180°C and 1200°C. The results are presented in table 5 and fig. 7. In the first three experiments of table 5, UCl₃ was not present in the salt phase. The distribution coefficients of Ce between molten U and BaCl₂ tabulated in table 5 are similar to those obtained in table 2:

$$K_D = 180 \text{ for U - BaCl}_2 \text{ at } 1180^\circ\text{C and}$$

$$K_D = 160 \text{ for U - BaCl}_2/\text{CaCl}_2 \text{ at } 1200^\circ\text{C}$$

With an increasing UCl₃ content in the salt phase the obtained distribution coefficients are greater by one to three orders of magnitude than those obtained with a neutral salt phase. In this case the following reaction should be therefore predominant:



and the corresponding equilibrium constant would be:

$$K = \frac{(\text{CeCl}_3^S) \cdot (\text{U}^m)}{(\text{Ce}^m) \cdot (\text{UCl}_3^S)} \quad (16)$$

The nomenclature remains the same as before.

TABLE 5

Coefficient K_D of Ce between liquid Uranium and the $BaCl_2/CaCl_2$ eutectic mixture as a function of the UCl_3 concentration of the salt phase

Temperature °C	UCl_3 in Salt Phase † %	Quantities				Equilibrium concentrations		Distribution coefficient $K_D = Ce_e^S / Ce_e^U$	Decontamination factor $F = Ce_a^U / Ce_e^U$
		Salt g	U g	Ce (U) mg	Ce_a^U mol %	$Ce_e^U \cdot 10^2$ mol %	Ce_e^S mol %		
1200	0	58,6	100,7	655	1,11	0,630	1,07	170	175
1200	0	34,9	131,7	1174	1,52	1,840	2,81	153	30
1200	0	47,7	90,1	890	1,68	1,002	1,61	184	168
1200	240	66,5	107,6	947	1,50	0,031	1,45	4610	4760
1180	512	70,2	94,1	834	1,51	0,011	1,35	11889	13301
1180	906	55,9	107,4	694	1,10	0,004	1,53	39231	28187

† The UCl_3 concentration is indicated in % of the quantity of U necessary for the oxydation of all the Ce present.

Evidence was found that the U metal formed in reaction (15) did not dissolve in the salt phase but joined the bulk of U metal phase.

Since the Ce concentration in the U metal phase was inferior to 10^{-4} mol %, this latter may be considered as pure U and consequently $(U^m) = 1$. Therefore the equilibrium constant simplifies to:

$$K = \frac{(CeCl_3^S)}{(Ce^m) (UCl_3^S)} \quad (17)$$

and introducing the activity coefficients

$$K = \frac{C_{CeCl_3^S} \cdot f_{CeCl_3^S}}{C_{(Ce)^m} \cdot C_{(UCl_3^S)} \cdot f_{(UCl_3^S)} \cdot C_{(ce)^m} \cdot f_{(UCl_3^S)^S}} \quad (18)$$

The equilibrium constant K may be calculated using the difference of the free energies of formation of UCl_3 and $CeCl_3$ at $1473^\circ K$ as given by Glassner [19]. The value obtained is:

$$K = 2.24 \times 10^5 \quad (19)$$

In equation (18) $C_{UCl_3^S}$ is well known and $f_{CeCl_3^S}$ may be estimated as explained in detail in 3.1.1 and 3.1.2 from the E.M.F. measurements of Senderoff [26] in $CaCl_2$ - $CeCl_3$ mixtures. The quotient $\frac{C_{CeCl_3^S}}{C_{Ce^m}}$ corresponds to the molar distribution coefficient K_D which is also known. The activity coefficients $f_{(Ce)^m}$ and $f_{(UCl_3^S)}$ are the only unknown, and their estimation is not possible now because of lacking literature data. However, the high value of the equilibrium constant which has been calculated above indicates that reaction (15) is shifted completely to the right and therefore $CeCl_3$ as well as U are formed at $1473^\circ K$. Finally we draw the conclusion that the experimentally obtained distribution numbers of Ce between U and the salt phase containing UCl_3 agree at least qualitatively with those theoretically expected.

3.4 The mass transfer rate of cerium

The results of the experiments for the determination of the mass transfer rate of Ce from the U metal phase to the salt phase are presented in table 6 and 7. In fig. 8 the mean slagging time is plotted as a function of the mean transfer rate per contact area. As a practical result we obtain a very useful slagging diagram. Example: for a chosen slagging time it will be

TABLE 6

The mass transfer rate of cerium from molten uranium into the salt phase

Experiment N. 162 Temperature: 1180 (°C) Salt species: BaCl₂/CaCl₂ eutectic mixture
containing 906% UCl₃⁺

Contact surface: F = 9,07 (cm²)

Quantities : 55,86 g salt, 107,38 g uranium containing 694 mg cerium

Slagging time	Mean sampling time	Remaining cerium	Passed cerium	Mean Transfer rate of cerium
t _n (min)	t _m = t _n + t _n / 2 (min)	G _n (mg)	G _n - G _{n+1} (mg)	R = $\frac{G_n - G_{n+1}}{t_m \cdot F}$ ($\frac{\text{mg}}{\text{min} \cdot \text{cm}^2}$)
2,5	1,25	47,5	646,5	28,57
11	6,75	2,168	45,33	0,576
55	33,0	0,633	1,535	3,8.10 ⁻³
122	88,5	0,104	0,529	0,87.10 ⁻³

⁺ The UCl₃ - concentration is indicated in (%) of the quantity necessary to oxidize all the cerium present.

TABLE 7

The mass transfer rate of Cerium from molten uranium into the salt phase

Experiment N. 151 Temperature: 1170(°C) Salt species: BaCl₂/CaCl₂ eutectic mixture

containing 70% UCl₃[†]

Contact surface: F = 9,07 (cm²)

Quantities: 62,1 g salt, 107,1 g uranium containing 697 mg cerium

Slagging time	Mean sampling time	Remaining cerium	Passed cerium	Mean transfer rate of cerium
t _n	t _m = t _n + t _n / 2	G _n	G _n - G _{n+1}	R = $\frac{G_n - G_{n+1}}{t_m \cdot F}$
(min)	(min)	(mg)	(mg)	($\frac{\text{mg}}{\text{min} \cdot \text{cm}^2}$)
1	0,5	536	339	37,5
3	2	176	360	19,87
12	7,5	3,33	172,67	2,12
132	72,0	0,94	2,39	2,2 · 10 ⁻³

[†] The UCl₃ - concentration is indicated in (%) of the quantity necessary to oxidize all the cerium present.

possible to determine the necessary contact area for a fixed transfer rate and a chosen salt species.

4. CONCLUSIONS

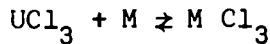
The extraction of cerium and lanthanum from molten irradiated uranium with a molten salt bath containing UCl_3 has been studied. Since this investigation was done in the framework of a Ph. D. thesis it was limited on these two fission products. However, it is reasonable to assume that the separation factors for the other Rare Earth Fission Products are very similar. Furthermore, since the alkaline and alkaline earth are even more electropositive than the RE metals, the separation through the slagging process should even be much better.

The use of $U^{235}Cl_3$ as a chlorinating agent seems to be very attractive. It was also stated that U^{235} losses in the salt bath going to the waste are negligible. From the given results and for a burn-up of 10% it is possible to obtain a Decontamination Factor of 3×10^4 for Ce and La under the following conditions: 1 Kg of irradiated U with 100 gr of UCl_3 in the slagging salt at $1250^\circ C$.

ANNEX

Practical application of the Halide Slagging

The results described in the present report are only concerned with Ce and La slagging at the equilibrium between uranium metal and a salt phase containing 1% of Ce and La. It is supposed that in the following examples the earth alkaline content of the salt phase does not change the equilibrium constant of the reaction:



M = alkaline earth

Determination of the decontamination Factor

In order to emphasize the practical interest of this work we will consider a few examples of a halide slagging reprocessing process. It should be noted that according to the above equilibrium reaction, the uranium of UCl_3 will be exchanged with a corresponding fission product. Therefore $U^{235} Cl_3$ will be used as an oxydating agent.

Calculation of the decontamination factor in a multiple Halide Slagging procedure

If we consider

X_2^0 = initial concentration of F.P. in U

X_2 = final " " "

C_1^0 = initial concentration of U in the salt

C_1 = final " " "

C_2 = final concentration of F.P. in the salt

P = the Nb of moles of U

N = the Nb of moles in the salt

M^0 = the Nb of moles of F.P.

m^0 = the Nb of moles of U in the salt

n = the number of performed halide slagging

D = decontamination Factor

(It is also supposed that the F.P. are trivalent and therefore 1 mole MCl_3 UCl_3).

$$K = \frac{C_2}{X_2 \cdot C_1} = C^{te}$$

However M° is transferred into the salt therefore

$$C_2 = X_2^{\circ} \cdot \frac{P}{N}$$

After the first halide slagging we have the relation:

$$C_1 = C_1^{\circ} - C_2 = (C_1^{\circ} - X_2 \cdot \frac{P}{N})$$

and

$$\frac{1}{X_2} = K \cdot \frac{C_1^{\circ} - X_2 \cdot \frac{P}{N}}{X_2^{\circ} \cdot \frac{P}{N}}$$

We have also $D = \frac{X_2^{\circ}}{X_2}$

and

$$D = K \cdot \frac{N}{P} \cdot (C_1^{\circ} - X_2 \cdot \frac{P}{N})$$

After n Halide Slagging

$$C_2 = n X_2^{\circ} \frac{P}{N}$$

$$C_1 = C_1^{\circ} - n X_2^{\circ} \cdot \frac{P}{N}$$

$$\frac{1}{X_2} = K \cdot \frac{C_1}{C_2} = K \cdot \frac{C_1^{\circ} - n X_2^{\circ} \cdot \frac{P}{N}}{n X_2^{\circ} \cdot \frac{P}{N}}$$

$$D = K \cdot \frac{N}{P} \cdot \frac{1}{n} (C_1^{\circ} - n X_2^{\circ} \frac{P}{N}) = K \left(\frac{C_1^{\circ}}{n} \cdot \frac{N}{P} - X_2^{\circ} \right)$$

D can be expressed in another form

$$D = K \frac{m^{\circ}}{nP} - \frac{M^{\circ}}{P} = \frac{K}{P} \left(\frac{m^{\circ}}{n} - M^{\circ} \right)$$

Practical conditions of the treatment

According to table 5, the value of the equilibrium constant $K = 200.000$ (medium value calculated from three results). Furthermore it is supposed that $m^{\circ} = P$ which means that the dissolved uranium amount in the salt phase at the start of the operation is equal to the uranium to be processed:

$$D = 200.000 \left(\frac{1}{n} - \frac{M^{\circ}}{P} \right)$$

We can now determine the number of halide slaggings which can be performed with the same salt bath in the following conditions:

$$\frac{M^{\circ}}{P} = 1\%; 3\%; \text{ and } 10\%$$

If M° represents all the Rare Earth and Alkaline Earth this corresponds roughly to 3%, 10% and 30% burn-up. In the equation $D = 200.00 \left(\frac{1}{n} - \frac{M^{\circ}}{P} \right)$, the value in parentheses must be positive. If this is the case, it will be possible to calculate the maximum number of slagging operations with one and the same bath.

$$M \text{ max} = 99 \quad \text{if} \quad \frac{M^{\circ}}{P} = 0,01$$

$$n \text{ max} = 33 \quad \text{if} \quad \frac{M^{\circ}}{P} = 0,03$$

$$n \text{ max} = 9 \quad \text{if} \quad \frac{M^{\circ}}{P} = 0,1$$

TABLE A-1

Calculated Decontamination factors as a function of n

	n = 1	n = 5	n = 9	n = 30	n = 90
$\frac{M^{\circ}}{P} = 0,01$	200.000	40.000	20.000	4.600	200
$\frac{M^{\circ}}{P} = 0,03$	200.000	34.000	16.000	6.000	-
$\frac{M^{\circ}}{P} = 0,1$	180.000	20.000	2.000	-	-

The above table gives an idea of the efficiency of the salt bath after n-sludging operations. It can be seen that the "D" is still very acceptable after 9 successive sludging operations in the same bath.

Halide Slagging with a Double Bath

If we consider the case of a halide slagging performed in a double bath (one salt bath followed immediately by a second one), the decontamination efficiency could be very high, since the total decontamination factor D_T will be equal to the product of D_1 and D_2 corresponding, respectively, to the first and second Halide Slagging.

In table A-2 below we give the calculated values of the performance of such a double bath. The total decontamination factors D_T are given as a function of M double slagging performance at different concentrations $\frac{M^O}{P}$. (0,01; 0,03; 0,1).

TABLE A-2

	n = 1	n = 5	n = 9	n = 30	
$\frac{M^O}{P} = 0,01$	$4 \cdot 10^{10}$	$1,6 \cdot 10^9$	$4,4 \cdot 10^8$	$3,2 \cdot 10^7$	4.400
$\frac{M^O}{P} = 0,03$	$4 \cdot 10^{10}$	$1,4 \cdot 10^9$	$3,5 \cdot 10^8$	$4,2 \cdot 10^6$	-
$\frac{M^O}{P} = 0,1$	$3,6 \cdot 10^{110}$	$7 \cdot 10^8$	$4,4 \cdot 10^6$	-	-

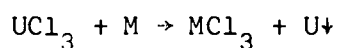
From this table we conclude that in the first two cases ($\frac{M^O}{P} = 0,01$ and 0,03) it is possible to perform 9 double halide slaggings in the same baths with still a very high D_T after the ninth operation. In the third case with $\frac{M^O}{P} = 0,1$ the same D_T is already reached after only $n = 5$. This means that in the latter case the slagging performance is a little less efficient, but still very acceptable.

From this theoretical consideration a practical conclusion can be derived, as far as the decontamination of the R.E. are concerned. The slagging bath could be used for about 10 successive slagging operations before it must be discarded as a solid waste.

Uranium recovery in the exhausted salt bath

The slagging operation will be performed with enriched uranium (U^{235}), therefore the bath should be completely exhausted before it will be discarded as waste.

As a practical example let us again consider a double bath slagging procedure with $N = 9$ successive operations. The bath Nr. 1 will be loaded with the bulk of the fission products and will contain still some enriched UCl_3 . The bath Nr.2 will be only slightly contaminated with fission products and therefore could be used as Nr.1 for the following series of slagging operations. The problem of the enriched U recovery remains only for the bath Nr.1. This uranium could be recovered easily by the following precipitation reaction:



M = inactive cerium

Operating conditions

A stoichiometric quantity of cerium metal will be added to the used bath, the uranium metal precipitates and goes to the liquid uranium already present. This precipitation reaction is facilitated by the fact that Ce is slightly soluble in the $BaCl_2 - CaCl_2$ salt bath and almost insoluble in liquid uranium.

Therefore, the uranium extraction of the discarded bath should not be of major concern.

ACKNOWLEDGEMENTS

The authors are indebted to Mr. P. Vanloo for his valuable cooperation concerning the radiochemical analyses. They wish to thank also the analytical chemistry team of Dr. G. Vos for the X-rays analyses. They are grateful to Dr. Scherff for his participation in the discussions.

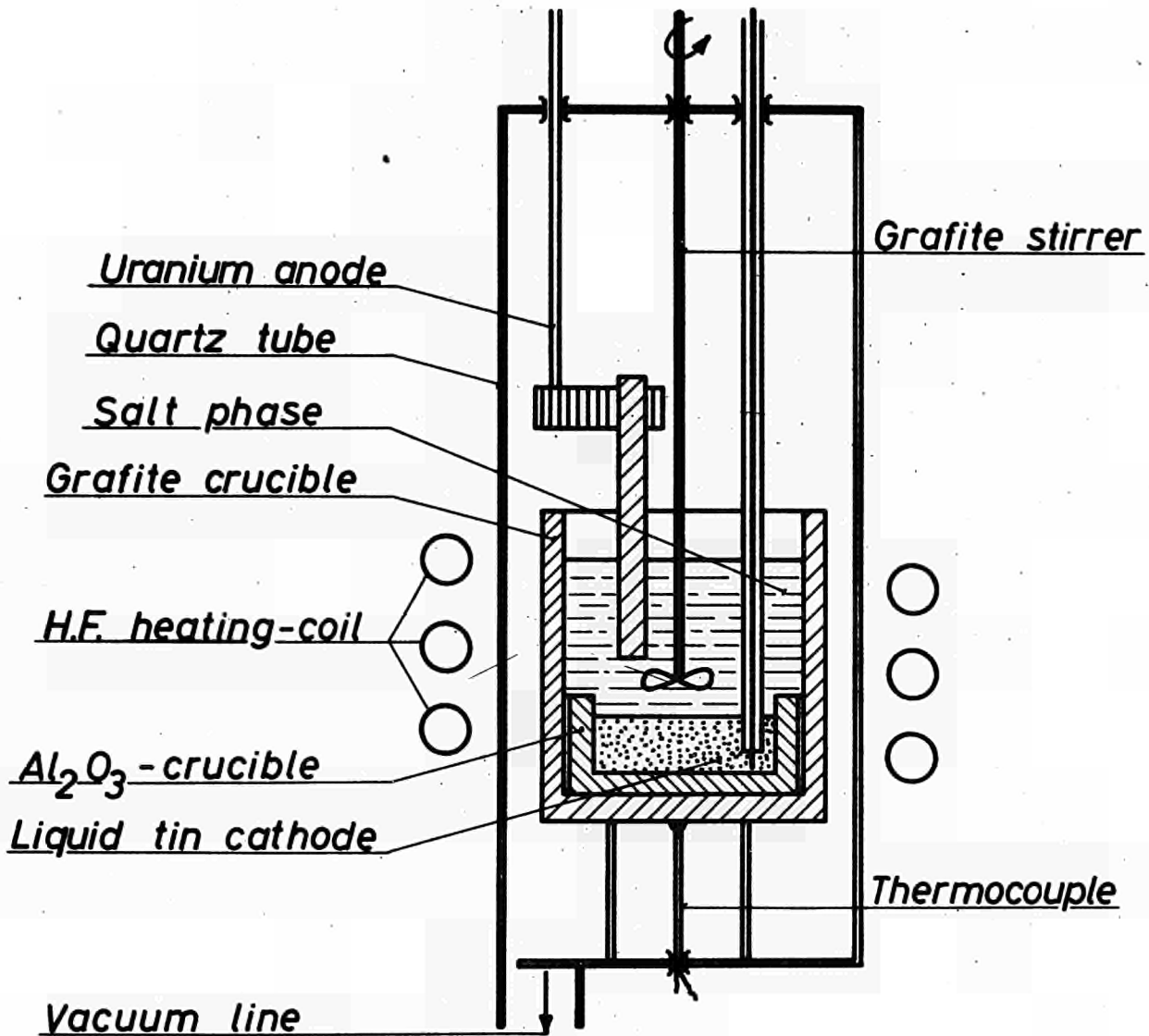
This work was performed as a part of the Ph.D.-thesis presented by Dr. G. Sennewald at the University of Braunschweig (W. Germany) under the high authority of Prof. Roland Lindner.

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PRODUCTION OF UCl_3 BY MEANS OF ELECTROLYSIS OF $AgCl$ INSIDE THE $BaCl_2$ - $CaCl_2$ EUTECTIC MIXTURE

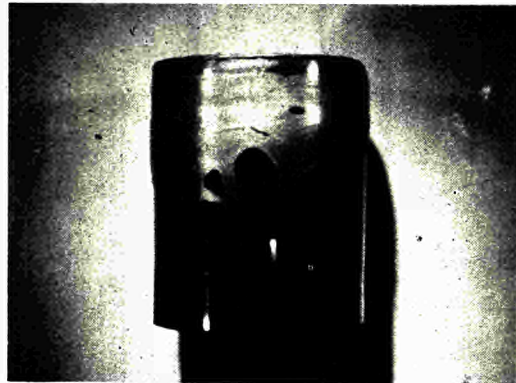


Working conditions : 700 (°C) ; 760 (Torr.) purified Argon
Salt phase : $BaCl_2$ - $CaCl_2$ - eutectic mixture containing
20 (wt.-%) $AgCl$

Figure 1



(a)



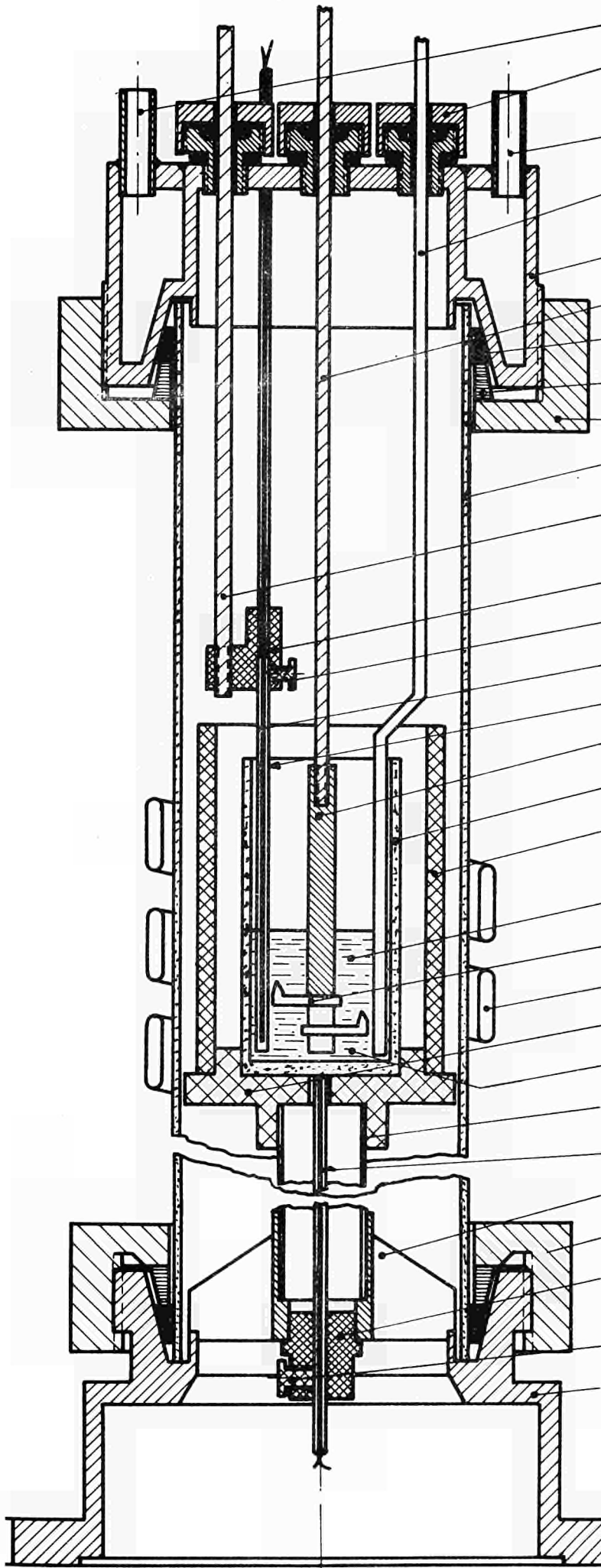
(b)



(c)

Fig.2 Tantalum crucibles made from 0,5 mm tantalum sheet after an equal contact time of 30 min. with liquid uranium at (a) 1140, (b) 1160 and (c) 1180°C. 1,5 natural size approx.

HALIDE SLAGGING APARATUS



- Cooling water entry
- Vacuum sealed passage
- Cooling water exit
- Quarz sampling tube
(4 tubes upon circumference)
- Water cooled Aluminium flange
- Stirrer support (steel)
- Trapezoidal rubber washer
- Steel ring
- Ring nut
- Quartz tube 100mm o.d.
- Steel rod supporting
thermocouple
- Intermediate piece (grafite)
- Grafite screw
- Thermocouple
- BeO - sheath
- Tantalum stirrer
- BeO - crucible
- Grafite shield as
HF susceptor
- Salt phase
- Tantalum stirrer blade
- HF coil
- Grafite plate
- Metal phase (uranium)
- Quartz tube as crucible support
- Thermocouple
- Steel support
- Steel nut
- Grafite support for
thermocouple
- Grafite screw
- Steel flange

Fig. 3

THE MOLAR SOLUBILITY OF Ce IN THE BaCl₂ - CaCl₂-EUTECTIC AS A FUNCTION OF THE ABSOLUTE TEMPERATURE.

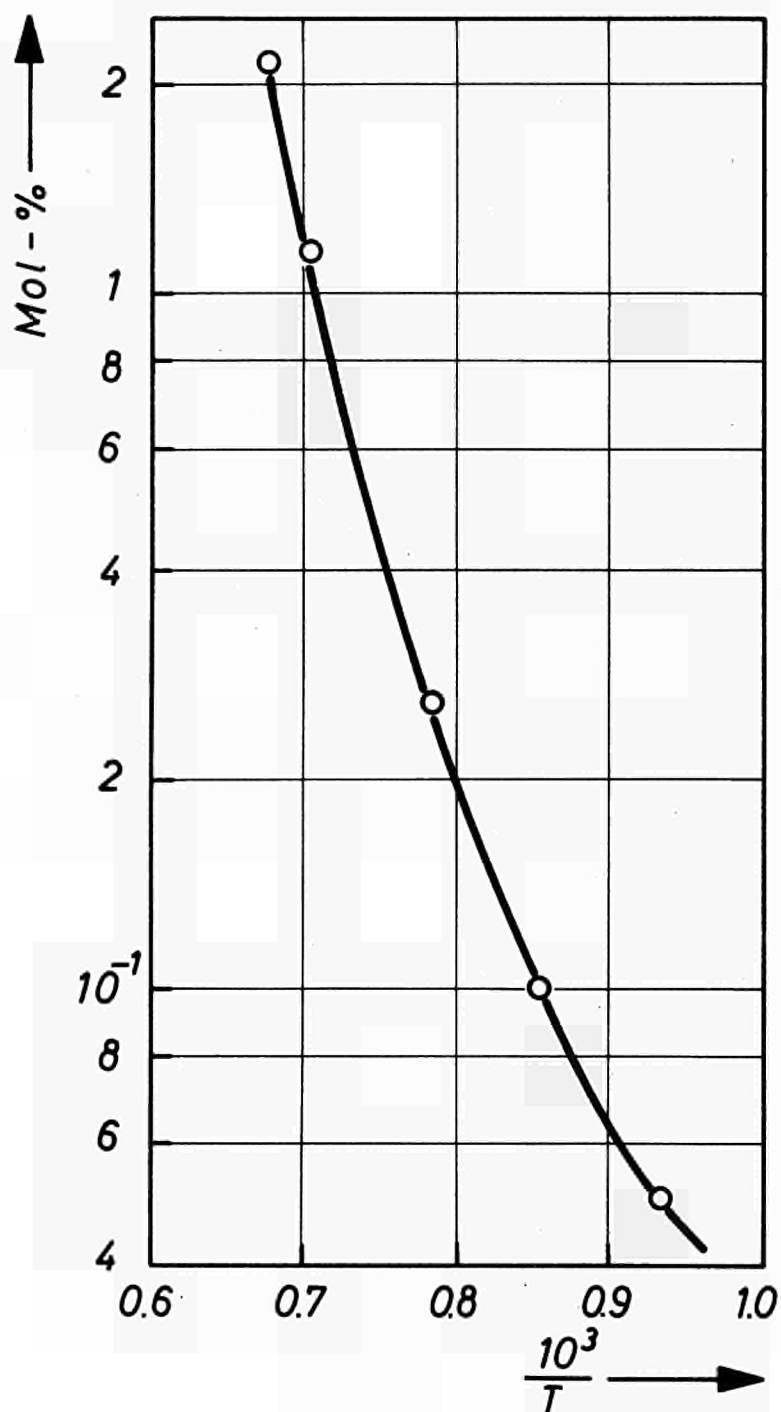


Figure 4

THE DISTRIBUTION OF La BETWEEN URANIUM AND BaCl₂ AS A FUNCTION OF TEMPERATURE ; INITIAL CONCENTRATION OF La IN U ca. 10⁻² (mol-%)

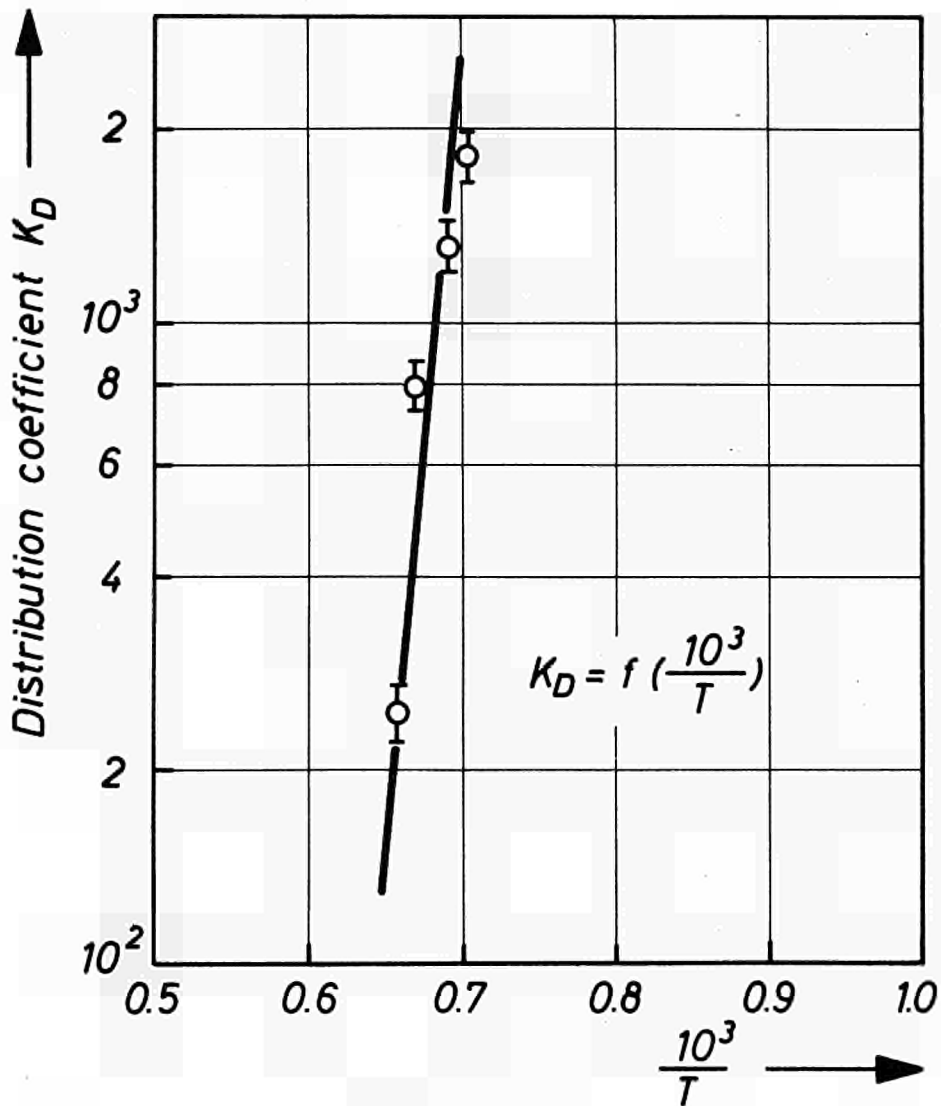


Figure 5

THE DISTRIBUTION OF Ce BETWEEN URANIUM AND BaCl₂ AS A FUNCTION OF TEMPERATURE ; INITIAL CONCENTRATION OF Ce IN U ca : 1.0 (mol-%)

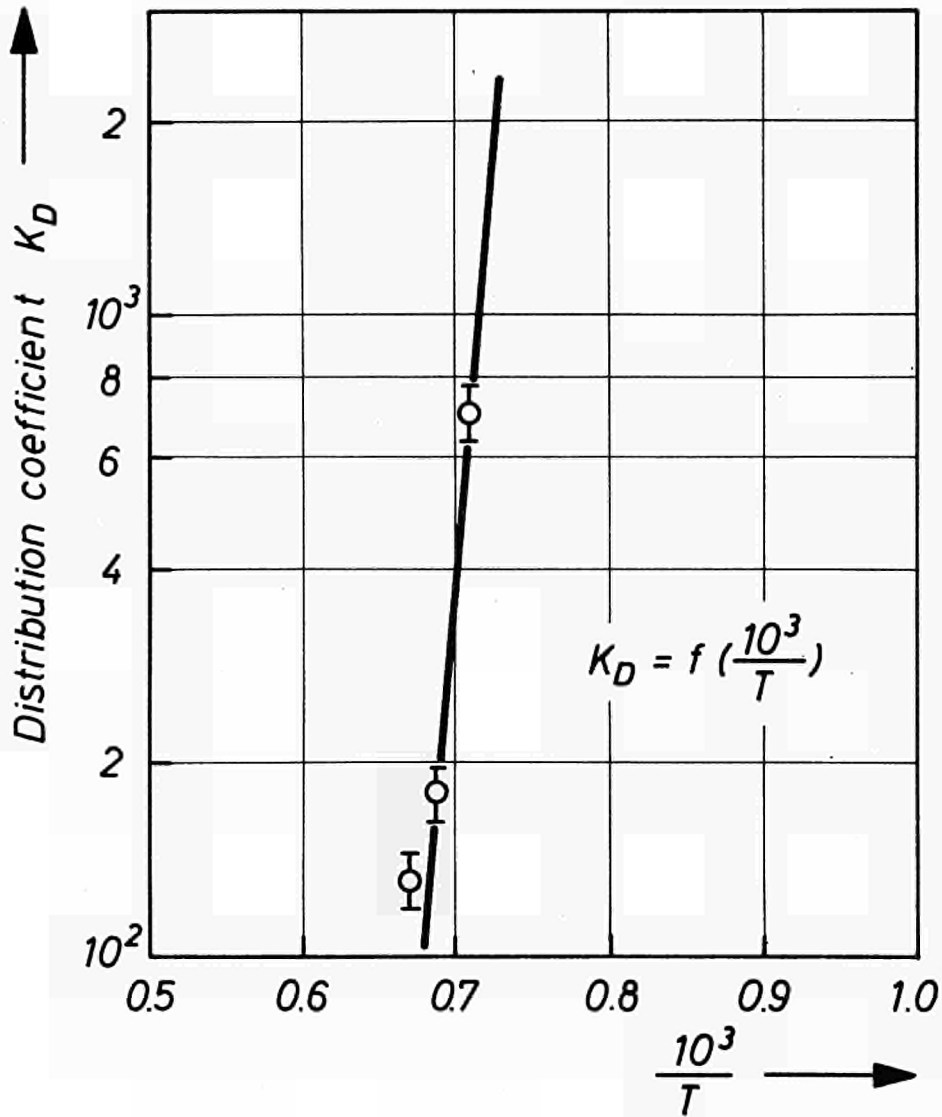


Figure 6

THE DISTRIBUTION COEFFICIENT K_D OF Ce VS. THE UCl_3 EXCESS CONCENTRATION OF THE SALT PHASE.

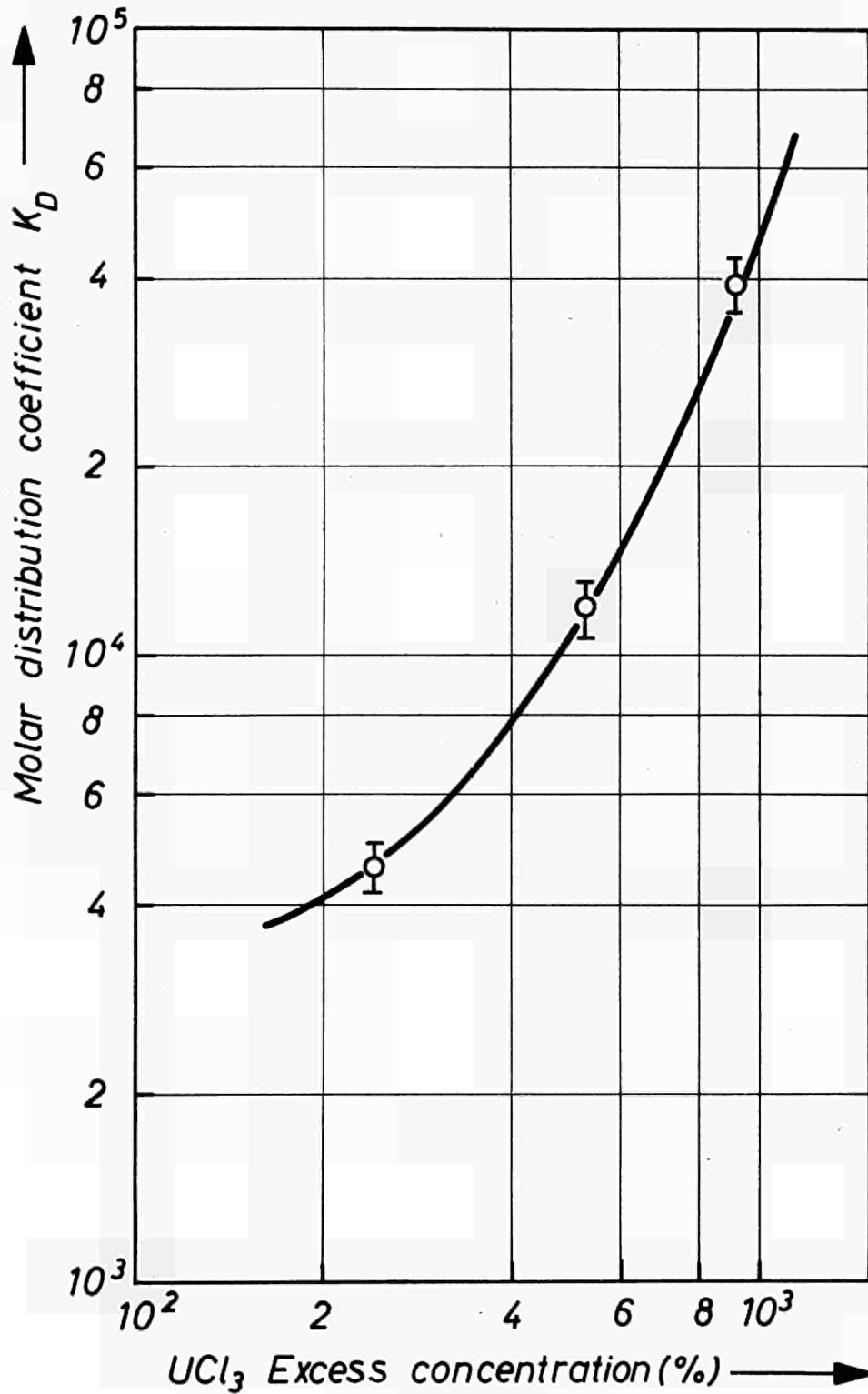


Figure 7

THE MEAN TRANSITION VELOCITY OF Ce VS. UCl_3 - CONCENTRATION OF THE SALT PHASE

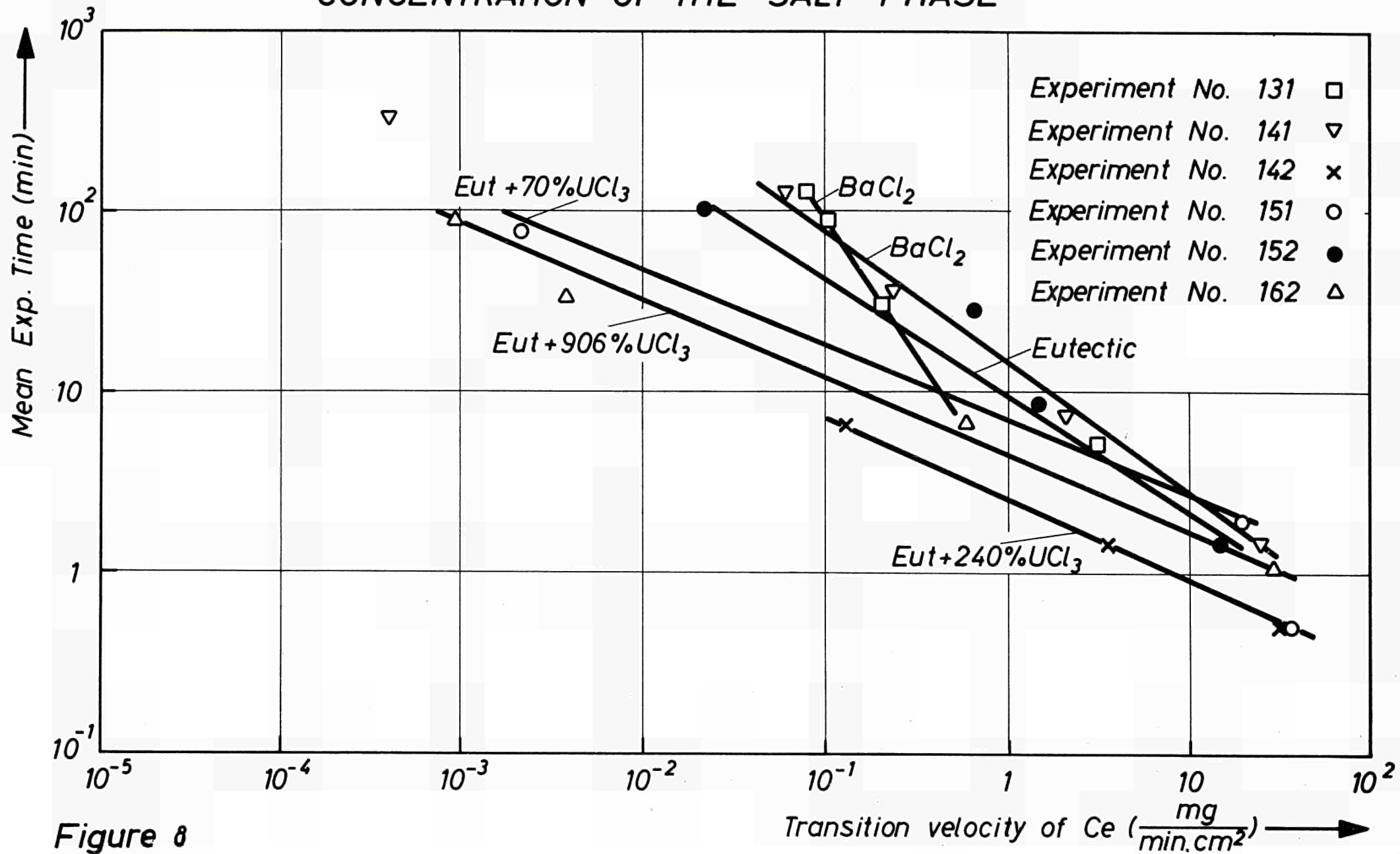


Figure 8

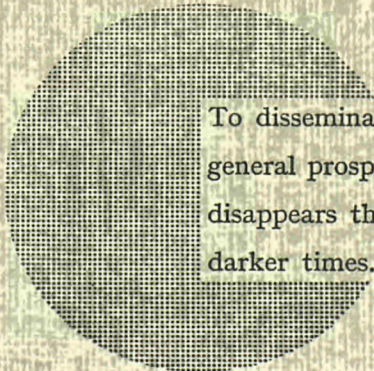
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Alfred Nobel

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