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Summary

1. The cementation of mercury as means for its removal from flue-gas scrub solutions has been tested in lab-scale. The experimental results have been used for the preliminary design of an industrial cementation reactor applying scrap iron shavings.

2. The results indicate that there is a lower limit (of about 0,35 mg/l) to the residual mercury concentration in the treated solution.
   This concentration is higher than the maximal permissible concentration for disposal (0.05 ppm). It complies, however, with the pre-treatment requirements for the 3R-process. High parasitic dissolution of iron indicate evolution of large quantities of hydrogen.

3. The design parameters of the cementation reactor complicate the mechanical requirements set by the need to replenish continuously the iron shavings hold-up in the reactor.

4. The cementation route for the removal of mercury from the flue-gas scrub solutions has therefore been found to be less attractive than expected.

Zur Quecksilberabtrennung aus Rauchgaswaschlösungen zur Zementation

Zusammenfassung

1. Die Abtrennung von Quecksilber aus Rauchgaswaschlösungen durch Zementation wurde im Labormaßstab erprobt. Auf der Basis dieser Versuchsergebnisse wurde ein Zementationsreaktor im großtechnischen Maßstab ausgelegt, in dem Eisenschrott für die Zementation verwendet werden sollte.

2. Die Versuchsergebnisse weisen eine minimale Quecksilberrestkonzentration von 0,35 mg/l aus. Diese Konzentration liegt erheblich höher als der übliche Einleitwert für Quecksilber in Vorfluter bei 5 mg/l. Er erfüllt aber die Qualitätsanforderungen für eine Quecksilbervorabtrennung im 3R-Prozess. Der hohe parasitäre Verbrauch an Eisen führt zu einer bedeutenden Wasserstoffproduktion.

3. Komplikationen bei der Reaktorauslegung ergeben sich durch die Notwendigkeit, den Verbrauch an Eisenspänen kontinuierlich zu ersetzen.

4. Die Zementation als Methode zur Quecksilberabtrennung aus Rauchgaswaschlösungen erwies sich somit weniger attraktiv erwartet.

1. Introduction

Cementation is a metal replacement process in which an ionized metal is displaced from its solution by spontaneous electrochemical reduction to the elemental metallic state, with subsequent oxidation of a sacrificial metal (such as iron). The reaction for mercury and iron is:

$$Hg^{+2} + Fe^{o} \dashrightarrow Hg^{o} + Fe^{+2} \qquad (1)$$

The result is to replace mercury with iron in the solution. The reduced mercury precipitates onto the solid iron surface.

In a preliminary study of electrochemical methods for the removal of mercury from the RGWW solution of the 3R-process, cementation has been pointed out as the potentially preferred alternative [1]. This choice was justified intuitively by its expected simplicity and by the expected very low costs of consumable resources needed for this process. It has further been pointed out that costs reduction can be achieved by using low cost iron sources (such as scrap or shavings), and that excessive iron consumption is expected due to parasitic dissolution in the acidic RGWW medium.

Although being an established industrial technology, the cementation of mercury at the specific conditions of the 3R-process was unfamiliar. Therefore, comparative evaluation of its characteristics and prospects with respect to other alternative processes was impossible. A "short-cut" experimental program has thus been carried out, aiming at getting some insight of the main features of the cementation process referring to its specific application for mercury removal from the RGWW solution.

The study summarized in this report included the following steps:

a) Experimental estimation of the kinetic parameters of the relevant reactions in the RGWW solution.

b) Experimental lab-scale study of the performance of a cementation column packed with scrap iron shavings.

c) Preliminary evaluation of major design factors of an industrial scale cementation column according to the results of a) and b).

From a scientific point of view, this study is by no means complete. The results gathered hitherto provide, however, a reasonable basis for a comparative screening evaluation. No further experimental work is therefore anticipated at this stage.

2. Background and previous work:

As stated above, cementation is a spontaneous electrochemical reaction driven by the EMF difference between the dissolved ionized metal and the sacrificial cementing metal.

Due to its high electropositive nature ($E^o = +0.851$ V) mercury ions can be cemented by almost every common metal. However, iron seems to be the most practical choice because of the following reasons:

a) Good availability of low cost iron, e.g. scrap.

b) It is a harmless pollutant as compared to other suitable metals like Zn, Cd, Cu and Ni.

c) It does not form an amalgam with mercury deposits, hence its surface remains uncoated and active.

The EMF difference for this metals couple (Fe/Hg) is +1.26 V. Application of the Nernst equation yields the following equilibrium-constant for the cementation reaction (1):

$$(2) \qquad K_{redox} = \frac{[Fe^{+2}]}{[Hg\ \ ]} = 10^{39.37} \qquad (T = 50^o\ C)$$

This enormously high value indicates that the electrochemical back-reaction (re-dissolution of already cemented mercury) is absolutely negligible for any reasonable value of $[Fe^{+2}]$.

The rate of the cementation reaction is a complicated function of the activation-overpotential characteristics of both metals and of the mass-transfer characteristics of the physical system [2].

The rigorous derivation of the kinetic equations is beyond the scope of this work.

Prior studies of other cementation systems [2] showed that for most cases, especially those having high EMF differences, the rate-determining-step is the mass-transfer of the cemented ions from the bulk of the solution to the surface of the cementing metal. In practice, it can therefore be assumed that the cementation reaction obeys a first-order rate law with respect to the dissolved metal concentration. Similar results have been obtained for the systems Cu^{++}/Fe [3, 4] and Pb^{++}/Fe [7].

The application of these findings to the case of the RGWW should be examined very carefully. Mass-transfer rate control implies the use of the following type of mathematical formulation:

$$(3) \qquad J = k\,(C_b - C_s)$$

where J denotes the flux of the cemented ions, C_b and C_s are its concentrations in the bulk of the solution and very close to the metal's surface respectively, and k is the mass transfer coefficient (being a function of diffusion coefficients and hydrodynamic conditions).

If $C_b \gg C_s$, the value of C_s can be neglected and the first-order rate law is obtained:

$$(4) \qquad J \propto kC_b$$

This approximation may be invalid at very low bulk concentrations, where C_s may be significant relative to C_b. Moreover, at the low concentration range, surface reactions and diffusion overpotential may become important rate controlling factors as well. Deviations from the first-order law are therefore expected at low concentrations, while cementation rates decrease asymptotically to zero as C_b approaches C_s.

Nadkarni and Wadsworth [3] who studied the system Cu^{++}/Fe, attributed such deviations from first-order rate to the built-up of copper on the iron surface thus increasing the diffusion path length. This explanation is probably invalid for the present case.

The other prevailing reaction, namely parasitic iron dissolution via reduction of hydrogen, stems from the acidity of the RGWW solution (pH ~ 1) and the electronegativity of iron ($E^o = -0.409$ V). The rate of iron dissolution by this reaction is probably controlled by transfer of H^+ ions to the metal's surface [5]. Because of the relatively high concentration of H^+, its consumption due to iron dissolution is insignificant. Therefore, this reaction can be regarded as having a zero-order kinetics with respect to the main components of the RGWW solution. This has been confirmed by Agelidis [7].

Minor transient deviations are, however, expected due to the presence of reducible species such as dissolved oxygen or Fe^{+3}. At its usual concentration range (5 ppm), Hg^{+2} should have no marked effect on the dissolution of iron.

The application of cementation in a packed column for wastewater treatment was discussed by Agelidis [8].

For the purpose of this work, the cementation of mercury and the dissolution of iron were assumed to have first and zero order kinetics respectively, without deviations. Hereafter, the experiments for estimating their rate constants are described.

3. Experimental

Two experimental systems, shown in Fig. 1, have been used for this study. The first one (system A) comprised of an iron tube (ID = 7.0 cm, length = 8.0 cm, thickness = 0.15 cm) placed in a glass vessel. Mixing of the solution took place inside the tube. Slots at its bottom enabled free liquid circulation throughout the vessel. Solution volume was 700 - 800 cm^3. Temperature was controlled by an electrical heating plate.

For the major part of the experiments, the outer side of this iron tube was covered by a polyethylene sleeve, so that only its inner surface area was available for cementation.

The second experimental system (system B) consisted of a glass column (ID = 2.2 cm, height = 16.0 cm), packed with iron shavings, taken from the LIT's workshop. The solution was circulated via a holding vessel at a rate of about 30 l/h.

The RGWW solution used for this experimental work was taken from the Bamberg MVA. Its mercury content was negligible because it has been treated by ion-exchange. Mercury was added to this solution by dissolving appropriate amounts of $HgCl_2$ (AR, Merck).

The experiments were carried out batchwise, by sampling and analysing concentrations as a function of time. Mercury was usually determined by Atomic Adsorption. Iron and high mercury concentration were determined by the TRFA.

4. Results

4.1 Cementation of mercury

As stated above, the kinetic parameters of the cementation reaction were measured using the mixed vessel system (A) which had a defined surface area. Results are shown in Fig. 2 and 3.

The straightline semilog plots of concentration versus time confirm the firstorder kinetics of this reaction for the "high" concentrations range. As expected, deviations from this rate law can be observed as the reaction proceeds and the "low" concentrations approach asymptotic values of a residual mercury concentrations.

The residual concentrations seem to be independent of the initial concentrations (and hence on the overall amount of precipitated mercury), but increase with increasing temperature. These phenomena give rise to the assumption that the residual bulk concentration, which is probably very close to the surface concentration C_s, results from the solubility of mercury in the RGWW medium.

The first-order rate constants derived from these results are summarized in table 1. Activation energy was calculated via the Arhenius plot shown in Fig. 4.

Table 1: First-order rate constants for the cementation of mercury with iron from RGWW

Temperature (° C)	Rate Constant (m/s)	Activation Energy (Kcal/g-mole)
22 ± 2	0.19×10^{-4}	
45 ± 2	*0.73×10^{-4}	9.6
60 ± 3	1.17×10^{-4}	

* Average of different initial concentrations (± 10%)

Similar phenomena have been observed with the packed column system B as well (Fig. 5 - 6). These measurements were applied for the estimation of the effective surface area of the iron shavings, assuming the same kinetic parameters for both experimental systems. The result is about 12.3 cm^2/g of shavings or about 1.8 cm^2/cm^3 of packed-bed column. This is only a rough estimate because of the unsimilar hydrodynamic conditions.

4.2 Dissolution of iron

As expected, the rate of iron dissolution in the RGWW solution during the cementation of the mercury follows approximately a zero-order kinetics shown in Fig. 7. Small deviations at the beginning of the process indicate higher initial rates, probably due to the presence of reducible substances (Fe^{+3}, dissolved oxygen, etc.) These enhanced initial dissolution rates become more prominent when the feed solution contains high concentrations of mercury. At that case, significant amounts of iron are consumed by the cementation which is imposed on the pure dissolution reaction (Fig. 8).

The pH dependence of the dissolution of iron was tested with acidified Bamberg RGWW solution. Hydrochloric acid AR was used for this purpose. Results are depicted in Fig. 9. Apparently, the "steady-state" dissolution rates shown in this figure indicate a very mild influence of the pH on the zero-order reaction-rate. However, the initial dissolution rates are very strongly affected by the pH. Lower pH-values produce significantly higher dissolution rates, resulting in an overall higher iron consumption. According to these results, the mechanism of the dissolution of iron which was discussed in paragraph 2 is probably incomplete and surface reactions may have an important role in controlling the reaction rate. For the purpose of the present study, a zero-order rate approximation is, however, sufficient.

The kinetic parameters of the dissolution of iron in the acidic RGWW solution as a function of the temperature are summarized in table 2. The rate constants are related to the zero-order kinetics. Activation energy was estimated via the Arhenius plot (Fig. 10).

Table 2: Kinetic parameters of the dissolution of iron in the RGWW solution (pH ~ 1.3)

Temperature (° C)	Rate constant (g/cm^2 s)	Activation energy (Kcal/g-mole)
22 ± 2	1.08×10^{-4}	
47 ± 2	2.2×10^{-4}	15
60 ± 3	2.7×10^{-4}	

4.3 Discussion of results

The results presented at the preceding paragraphs support the qualitative model which was evaluated as the theoretical background (§ 2).

The cementation of mercury has been found out to follow a first-order rate law with respect to the concentration of mercury at the "higher" concentrations range. Slow down of the reaction and hence a deviation from the first order kinetics are observed at the "lower" concentration range. According to the available data, the deviation becomes significant at concentrations below 0.7 - 0.8 mg/l at the temperature range of 45° - 60° C.

The asymptotic residual mercury concentration of about 0.25mg/l and 0.35 mg/l (at 45^o and 60^o C respectively) set an upper limit to the efficiency of the cementation method as means for removing mercury from the RGWW solution.

A high initial concentration of mercury was used to simulate highly loaded iron packing as expected for prolonged continuous operation of an industrial system (Fig. 8). A good removal efficiency has been found. However, observation of the outflowing solution showed suspended material, probably caused by carryover of cemented mercury. Filtration of the treated solution is therefore needed for an industrial cementation system.

The parasitic dissolution of iron via hydrogen reduction generally follows zero-order kinetics. The consumption of iron by the cementation itself is negligible when compared to its parasitic dissolution.

The kinetic data thus obtained have been used to estimate the design parameters of an industrial size cementation column, in order to evaluate the practical feasibility of the process.

5. Evaluation of a cementation reactor

5.1 Basic design parameters

For the preliminary design of an industrial cementation reactor packed with iron shavings, it is assumed that the reaction kinetics follows exactly the first-order rate law. However, confining the design data to the appropriate concentrations range imposes a practical limit of around 80 - 90% on the mercury removal efficiency at the usual feed concentration range (~ 5 ppm). Because of the slowing down of the reaction rate at lower concentrations, exceedingly higher reactor volumes will be needed for further efficiency improvements. Although being relatively low, such efficiencies should be sufficient for the purpose of the 3R-process.

Following this assumption, the time dependent behaviour of a batch cementation reactor (e.g. experimental systems A and B) can be described by the following equation:

$$(5) \qquad C = C_o\, e^{-\frac{kaVt}{V}}$$

while the steady tate behaviour of a continuous tubular reactor is:

$$(6) \qquad C = C_o\, e^{-\frac{ka\,SL}{Q}} = C_o\, e^{-\frac{kaV}{Q}}$$

The following notations were used:

C - mercury concentration (mg/l)
t - time (s)
k - first order rate constant (cm/s)
a - specific active surface area of the reactor (cm^2/cm^3)
V_R - reactor volume (cm^3)
V - solution volume (cm^3)
Q - solution flow rate (cm^3/s)
S - reactor cross section (cm^2)
L - reactor length or height (cm)

Equation (6) is the scale-up relationship for estimating the volume of a full-scale continuous cementation column. The fundamental parameter must be estimated from the lab column time-concentration curve by using eq. (5).

A more direct scale-up method can be evaluated provided the same feed solution is used for both experimental and the industrial columns. In that case, the exponents of both eq. (5) and (6) can be equated:

$$(7) \qquad \frac{V_{R1}t_1}{V_1} = \frac{V_{R2}}{Q}$$

where the subscripts 1 and 2 denote the batch experimental column and the full-scale column respectively. This equation provides a direct similarity relationship between both columns at the same removal efficiency.

It must be emphasized again that the above stated discussions along with eq. (5) to (7) are valid and applicable only at the first-order kinetics range.

5.2 Sizing a full-scale cementation column

The nominal performance requirements for estimating the size of a full-scale cementation column is based on the average Oberhausen MVA operating data:

$$Q = 7000 \text{ l/h} = 2 \text{ l/s}$$
$$C_o = 5 \text{ mg/l}$$

The calculations were carried out for Hg removal efficiencies of 80% and 90% and for the temperatures 45° and 60° C. The re-sults which have been obtained using the procedures outlined in the preceding paragraph are summarized in table 3.

These results are based on the data which were directly obtained by the experimental system B, with a circulation rate of around 30 l/h. This means that the superficial flow velocity through the lab column was about 2.2 cm/s. This figure determines the required cross-section of the full-scale column and hence it diameter. The required cross section for the nominal flow-rate of the RGWW is thus 910 cm^2, the diameter thus being about 34 cm. The active length of the column (or its height) is readily estimated and presented as well in table 3.

The effect of flow velocity of the RGWW solution on the size of the cementation reactor can be approximated by using the well-known power-law dependence of the mass-transfer coefficient on the velocity:

$$(8) \qquad k \propto u^n$$

For a packing having similar structure as the iron shavings, it has been measured that $n \approx 0.8$, at the relevant velocity range [6]. As the cementation process is mass-transfer controlled, it can be reasonably assumed that the (ka)-value is also proportional to $u^{0.8}$. According to eq. (6), the required reactor volume is inversely proportional to (ka) and hence

$$(9) \qquad V_R \propto u^{-0.8}$$

For a given flow-rate of RGWW Q, the cross-section area of the reactor is proportional to 1/u, hence its height is proportional to $u^{0.2}$.

A sample calculation of the influence of the linear velocity on the dimensions of the cementation reactor is shown in table 4. It is clearly seen that the reactor volume increases significantly when the flow-rate decreases. Its dimensions, however, become more reasonable for practical operation.

5.3 Consumption of iron

The dissolution of iron in the acidic RGWW solution has been shown to proceed according to a zero-order rate law. Because of the relatively high concentration of H^+, the mass-transfer effect is expected to be much less pronounced than in the case of cementation. Therefore, it can be assumed that the specific rate of iron dissolution is approximately constant for a given temperature, while all other parameters may vary in the range discussed in the preceding paragraphs.

Consequently, the absolute rate of iron dissolution is proportional to the active (or effective) volume of the cementation reactor.

Based on the hitherto estimated reaction rates presented in table 2, and the calculated specific surface area of the iron shavings packing (1.8 m^2/m^3), it can be evaluated that the iron dissolution rate R per m^3 packing is:

$$R = 14.30 \frac{kg}{h \cdot m} \quad \text{at } 45^o$$

$$R = 17.50 \frac{kg}{h \cdot m} \quad \text{at } 60^o$$

For the sample reactor present in table 3, iron consumption will be around 4 - 5 kg/h if the mercury removal efficiency is 90%. The additional iron concentration at the outlet stream will thus be around 600 - 700 mg/l.

This rate of iron consumption comprises about 10% of the iron hold-up of the reactor per hour. Consequently, special mechanical devices must be installed for replenishing the consumed iron continuously.

5. Conclusions

The short cut experimental program described in paragraphs 3 and 4 led to the design figures of a cementation reactor, presented in paragraph 5.

The design figures shown in tables 3 and 4 consider a high reactor with a small diameter. Such a design would be excellent for a normal column. In that case, the need for continuous or

frequent replenishment of the consumed iron shavings renders this design to be impractical, because of expected mechanical problems. Decreasing the flow-rate through the column results in a larger and more practical diameter. The volume increases, however, as well implying an undesired increased parasitic iron consumption.

Table 3: Nominal Size of a Full-Scale Cementation Reactor for the Removal of Mercury

Nominal operating conditions: $Q = 2$ l/s
$C_o = 5$ mg/l
$u = 0.022$ m/s

Temperature (°C)	Removal Eff. (%)	(ka)-value (s^{-1})	V_R (m^3)	L (m)	D (m)
45	80	0.0135	0.238	2.61	0.34
	90		0.345	3.80	0.34
60	80	0.0217	0.148	1.62	0,34
	90		0.212	2.33	0.34

Table 4: Calculated Effect of Flow Velocity on the Size of the Cementation Reactor

Removal Efficiency: 90%

	T = 45° C			T = 60° C		
U (m/s)	V_R (m^3)	L (m)	D (m)	V_R (m^3)	L (m)	D (m)
0.0330	0.250	3.50	0.28	0.153	2.15	0.28
0.0220*	0.345	3.80	0.34	0.212	2.33	0.34
0.0110	0.600	4.36	0.48	0.369	2.67	0.48
0.0055	1.045	5.01	0.668	0.642	3.07	0.68

* Base values, based on direct measurements.

The experimental results indicate also that there is a lower limit (about 0.35 mg/l) to the residual mercury concentration in the treated solution. This concentration does not comply with the regulations for wastewaters disposal (<0.05 mg/l). It suits, however, the pre-treatment requirements for the 3R-process.

Decreasing the linear flow velocity through the column results in enlarged diameter, which is much more practical. It results, however, with considerably increased reactor volume which leads to higher consumption of iron, higher iron concentrations in the outflowing streams and excessive hydrogen evolution.

Concluding this report, it can be said that the cementation process for removal of mercury from the RGWW solution is not so attractive as previously expected. A more rigorous comparison with other processes will be discussed in a following report.

Summary

1. The cementation of mercury as means for its removal from flue-gas scrub solutions has been tested in lab-scale. The experimental results have been used for the preliminary design of an industrial cementation reactor applying scrap iron shavings.

2. The results indicate that there is a lower limit (of about 0,35 mg/l) to the residual mercury concentration in the treated solution.
   This concentration is higher than the maximal permissible concentration for disposal (0.05 ppm). It complies, however, with the pre-treatment requirements for the 3R-process. High parasitic dissolution of iron indicate evolution of large quantities of hydrogen.

3. The design parameters of the cementation reactor complicate the mechanical requirements set by the need to replenish continuously the iron shavings hold-up in the reactor.

4. The cementation route for the removal of mercury from the flue-gas scrub solutions has therefore been found to be less attractive than expected.

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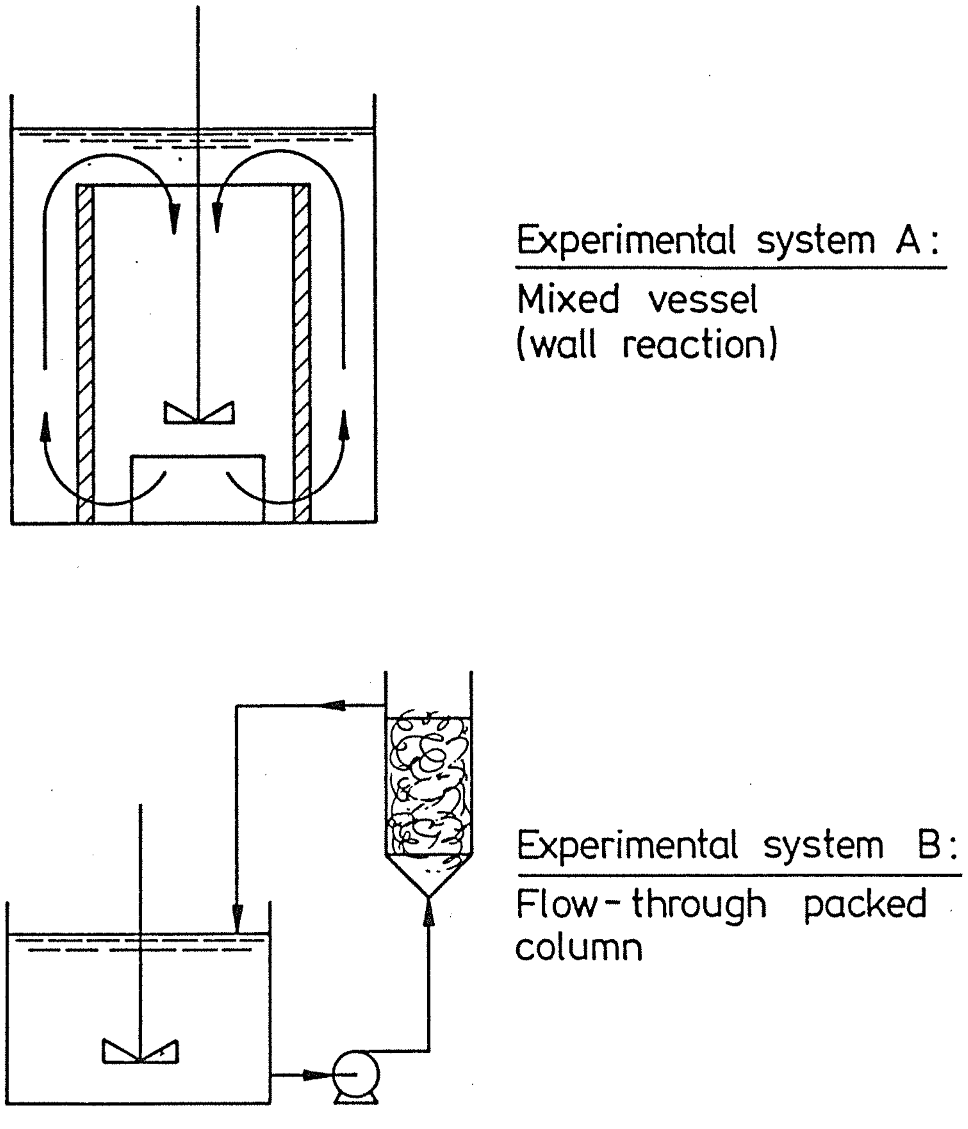

Fig. 1: Experimental set-ups for cementation studies

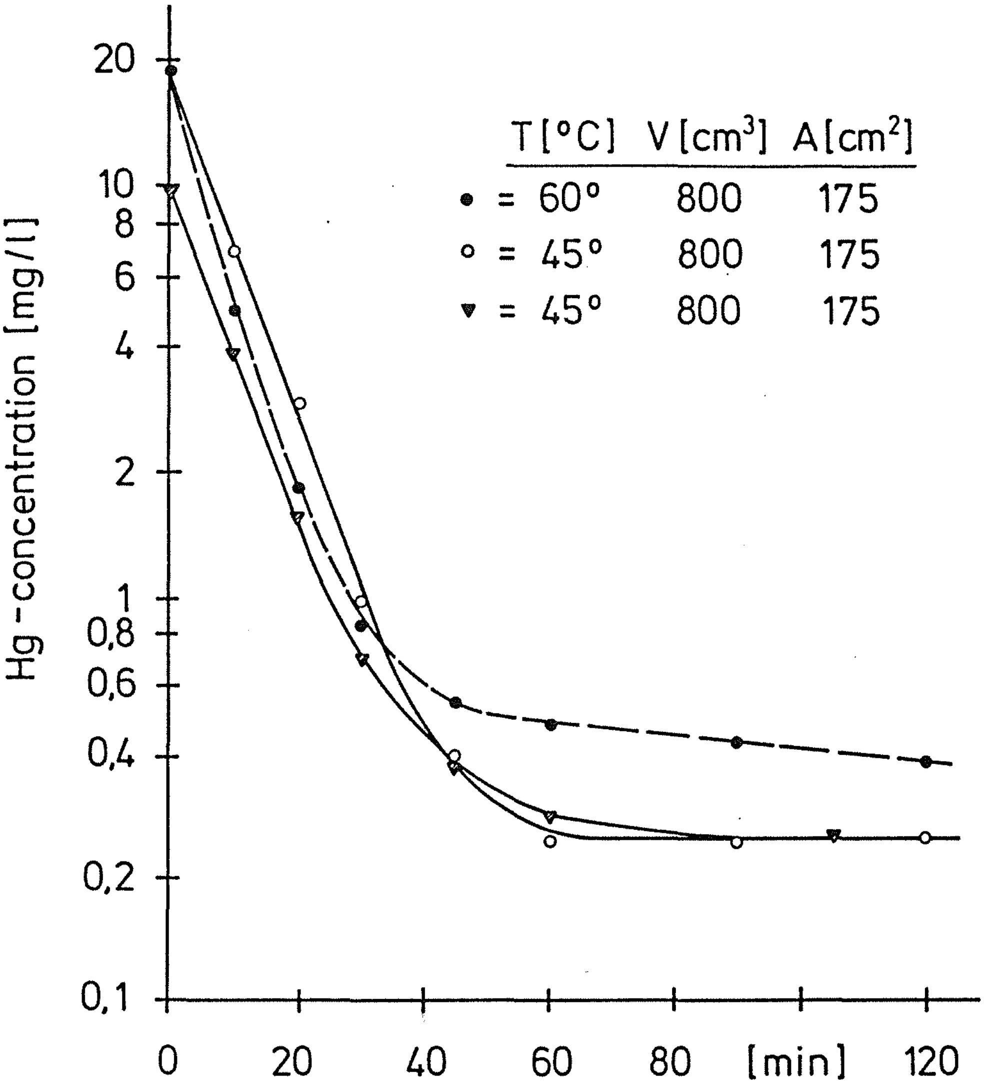

Fig. 2: Time-concentration plots for the cementation of **mercury**. Experimental system A. Active surface area: 175 cm^2 (coates iron tube)

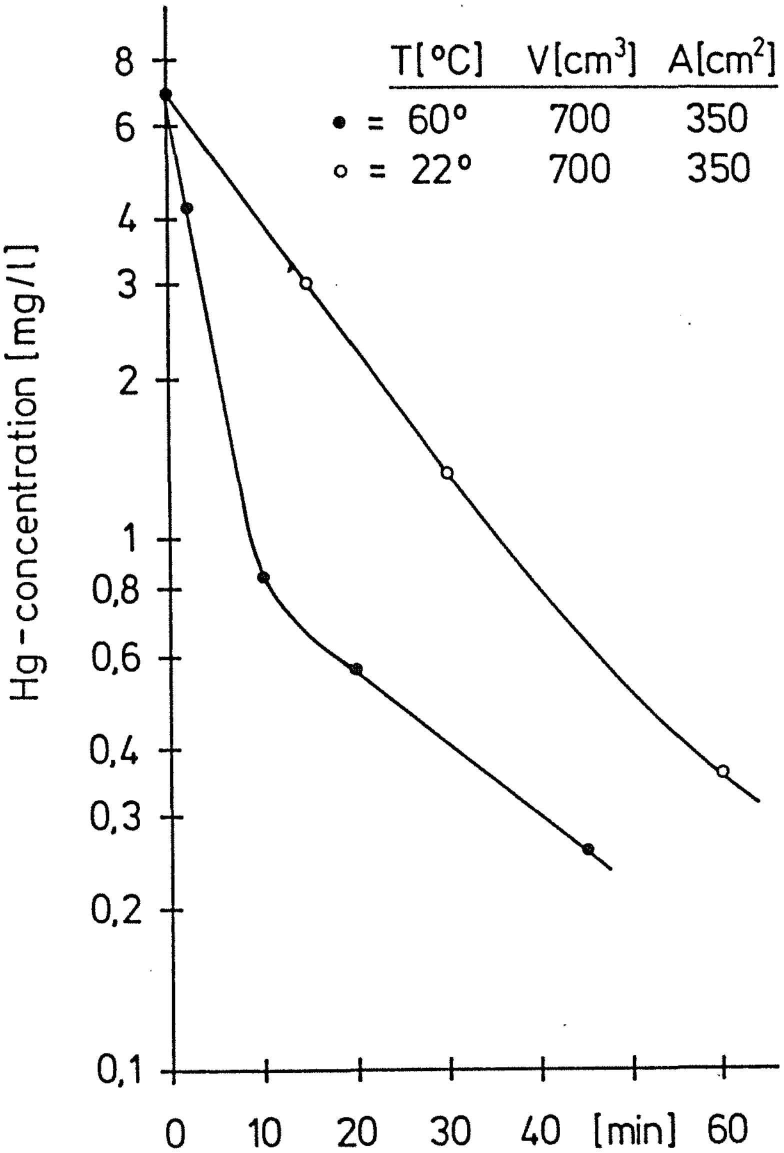

Fig. 3: Time-concentration plots for the cementation of mercury. Experimental system A. Active surface area: 350 cm^2 (uncoated iron tube)

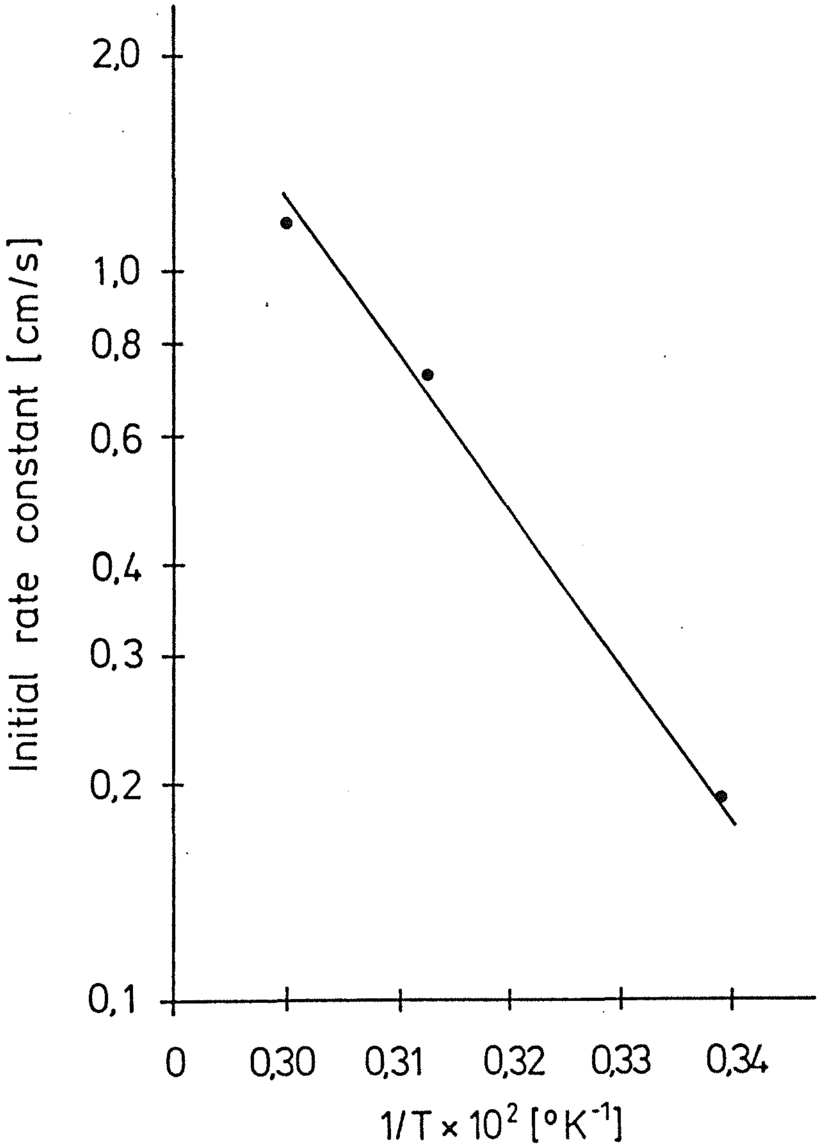

Fig. 4: Arhenius plot for the first-order part of the cementation reaction

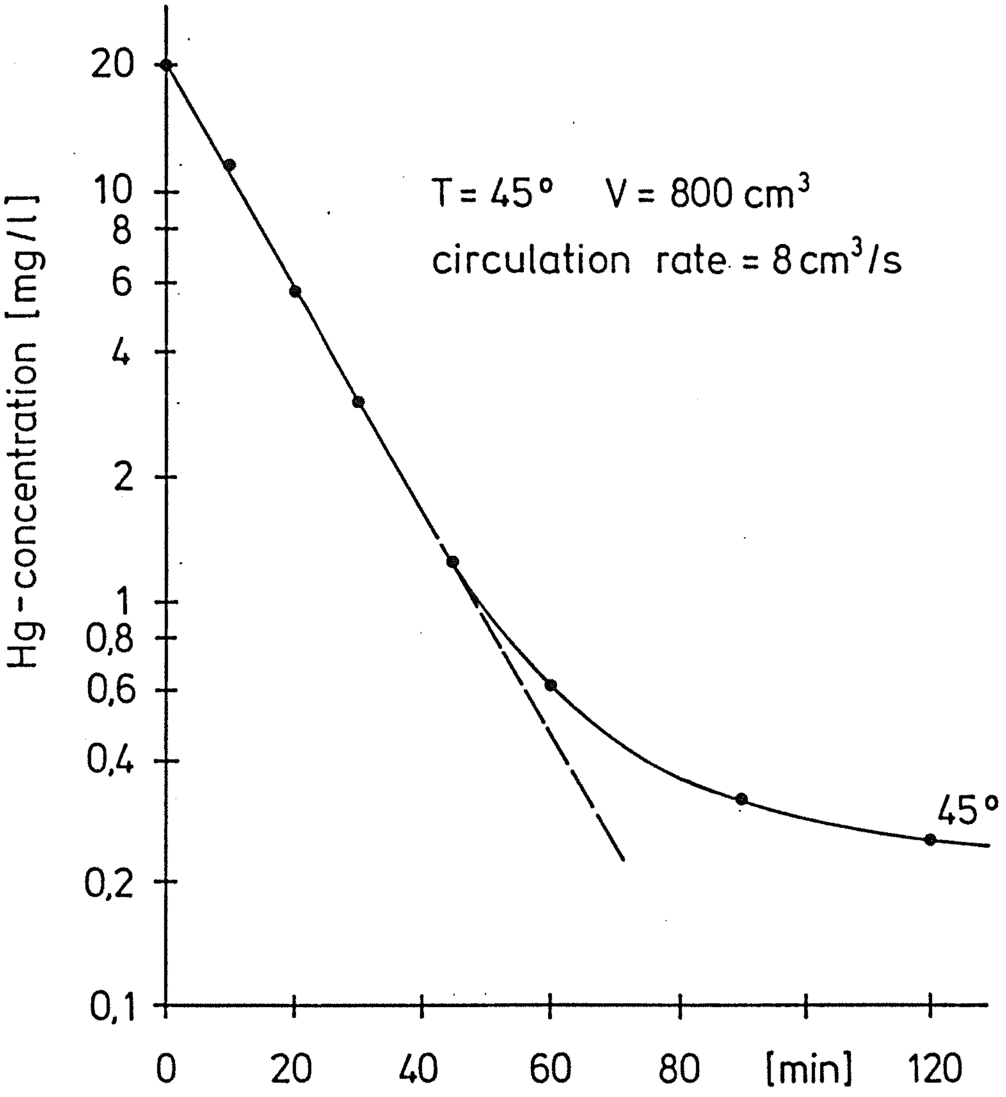

Fig. 5: Time-concentration plot for the cementation of mercury. Experimental system B (packed column). Initial Hg-concentration: 18.7 mgr/l Circulation rate through the column: 30 l/h

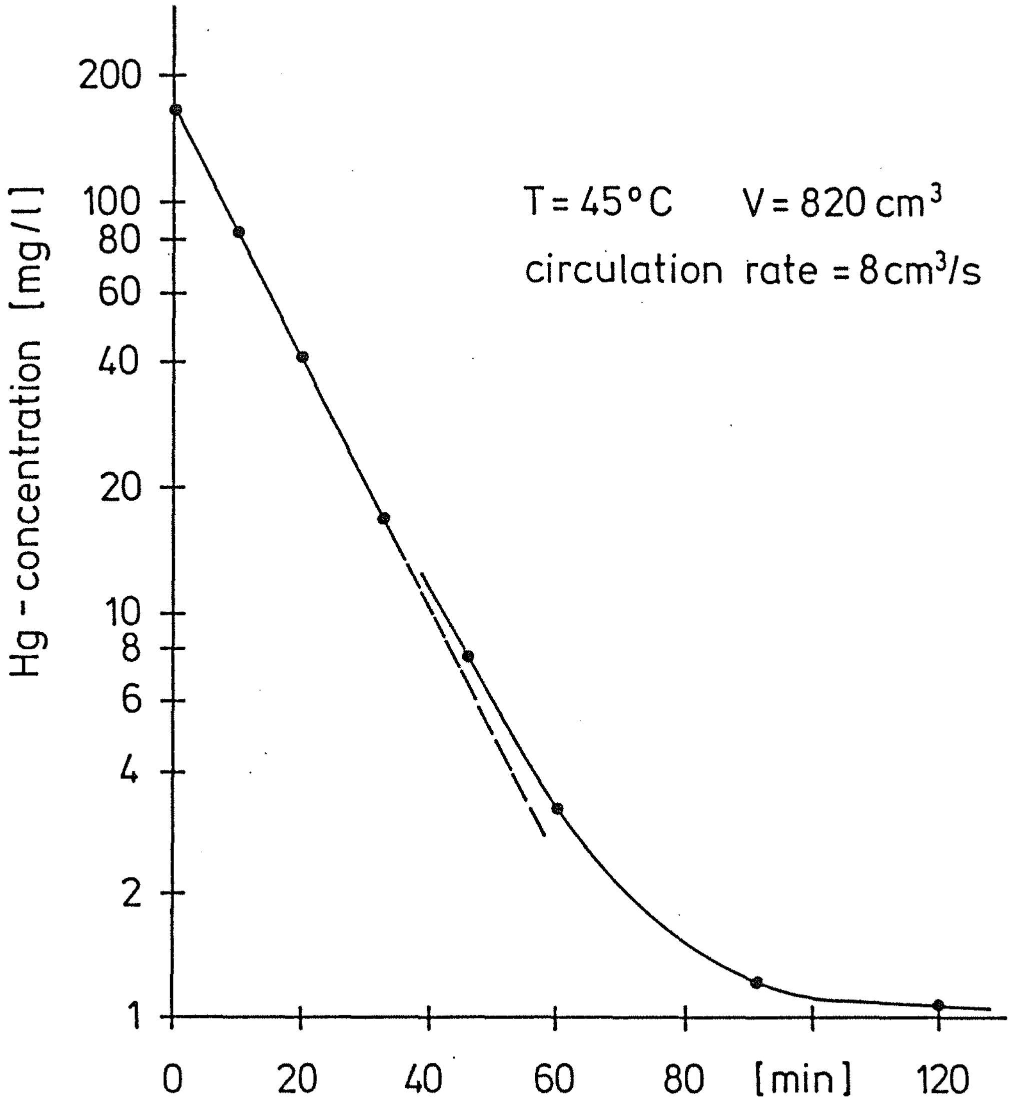

Fig. 6: Time-concentration plot for the cementation of mercury. Experimental system B (packed column). Initial Hg-concentration: 165 mgr/l Circulation rate: 30 l/h

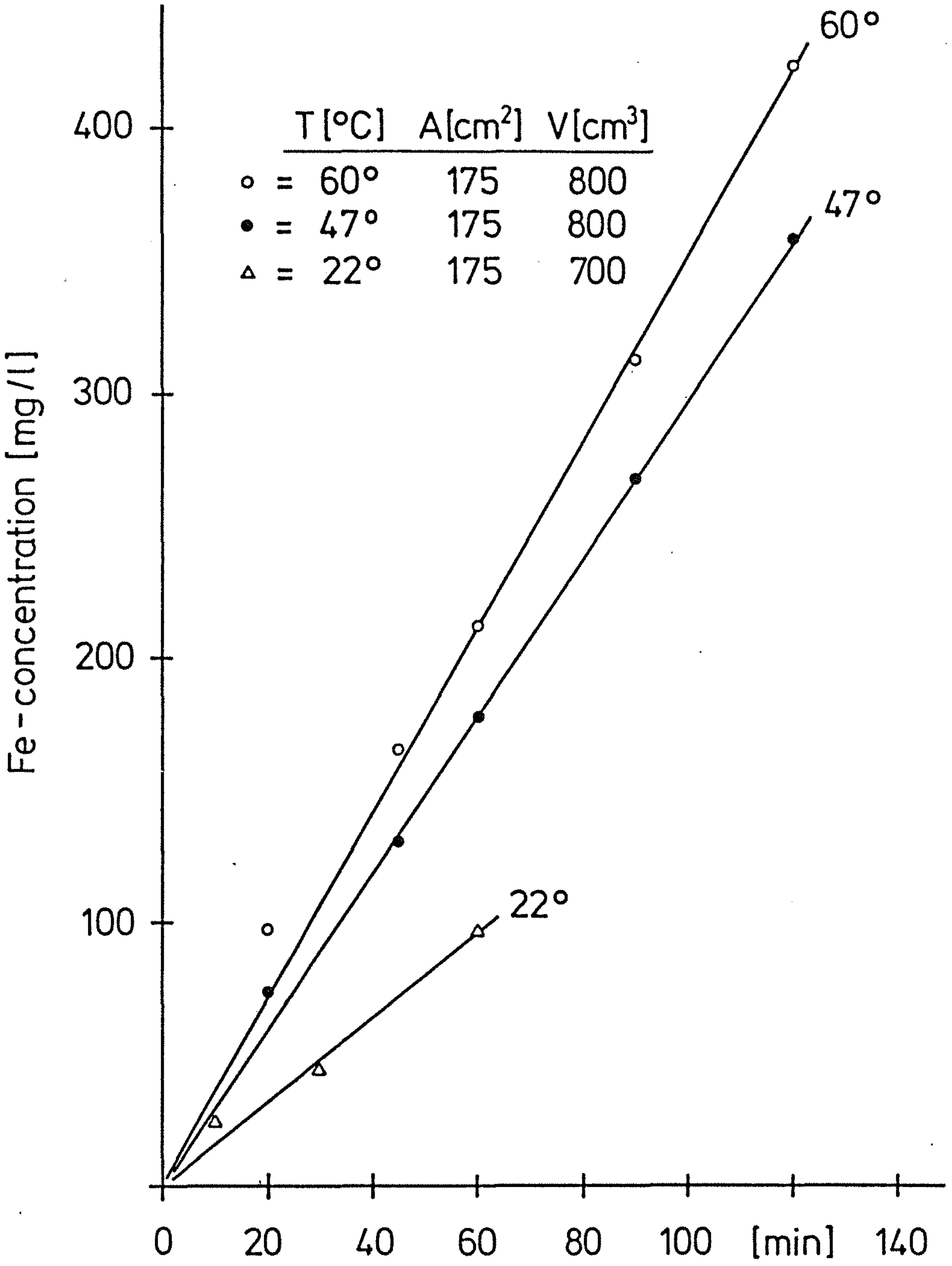

Fig. 7: Dissolution of iron. Experimental system A (pH = 1.3)

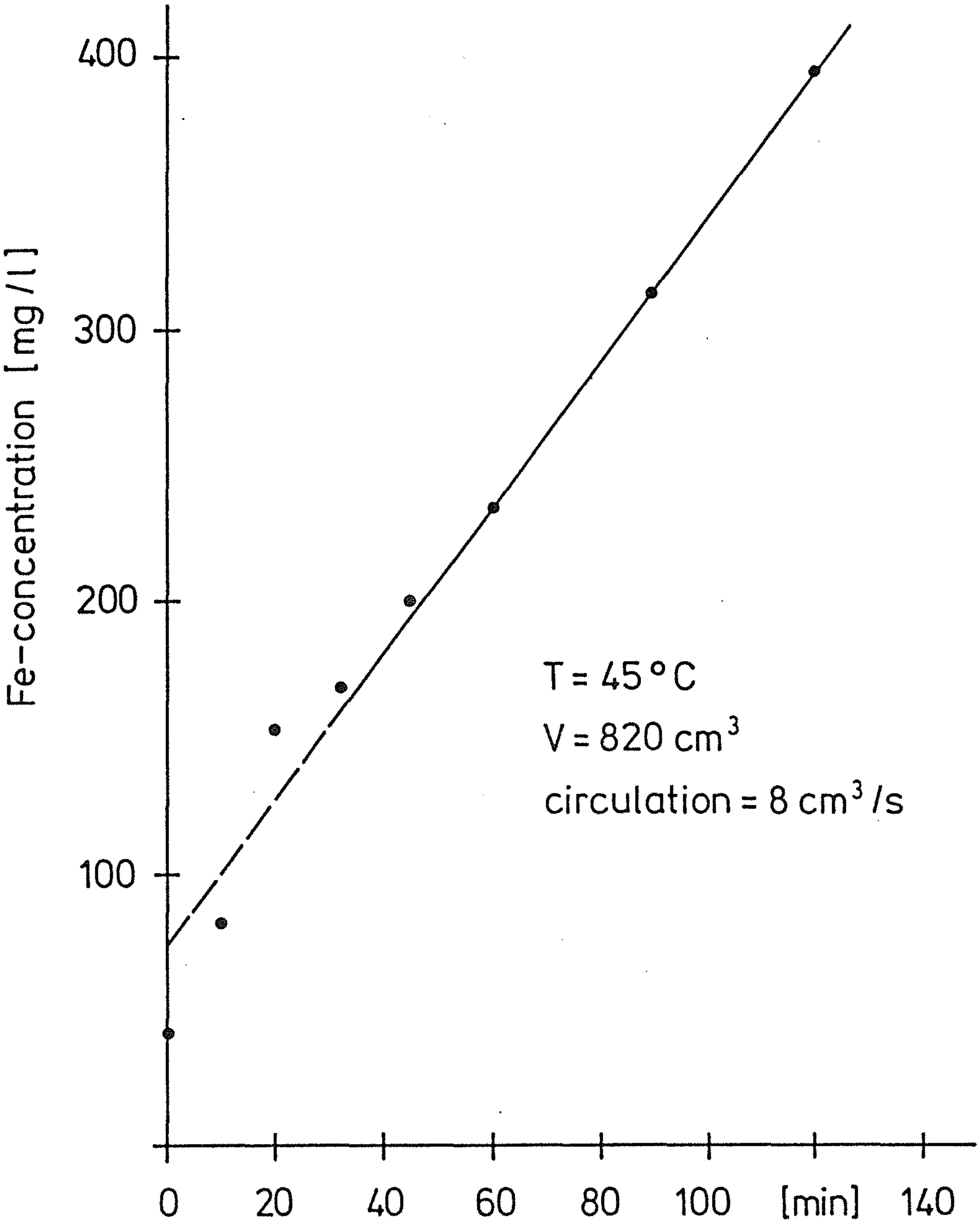

Fig. 8: Dissolution of iron. Experimental system B. High initial Hg-concentration (165 mg/l), pH = 1.3

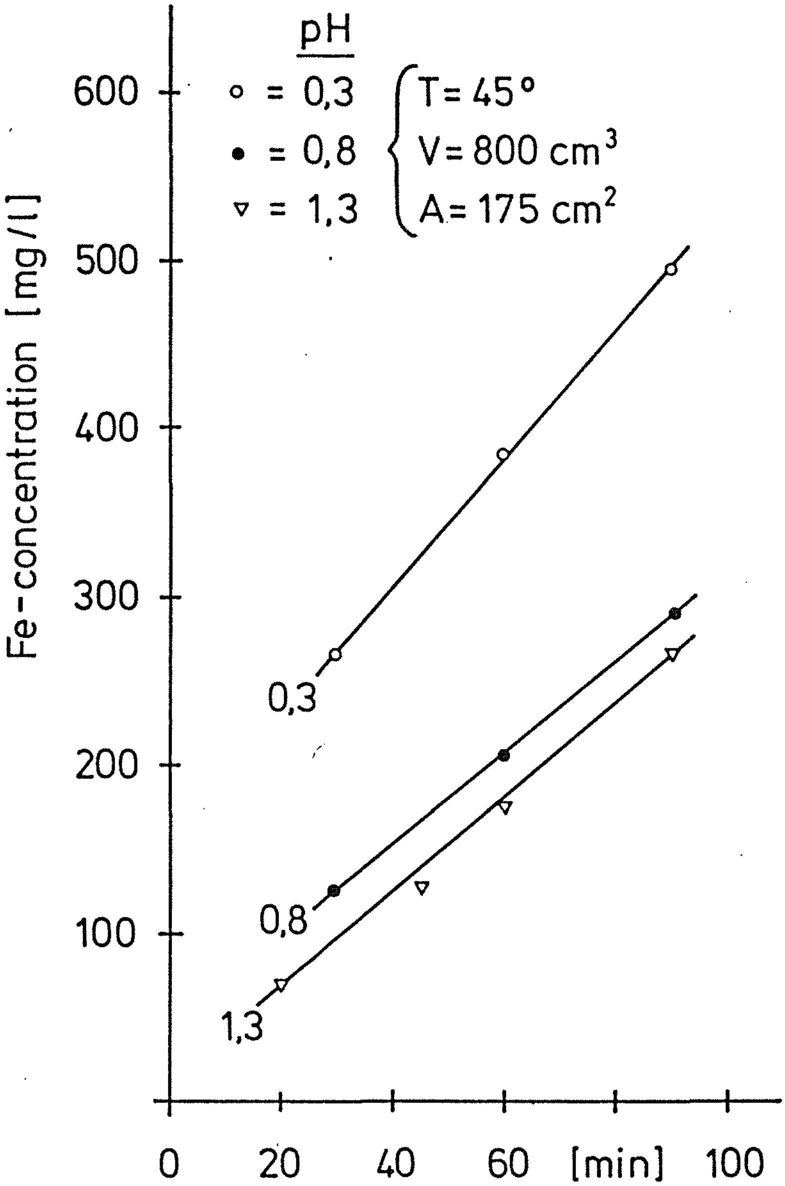

Fig. 9: Dissolution rate of iron as a function of pH. Experimental system A

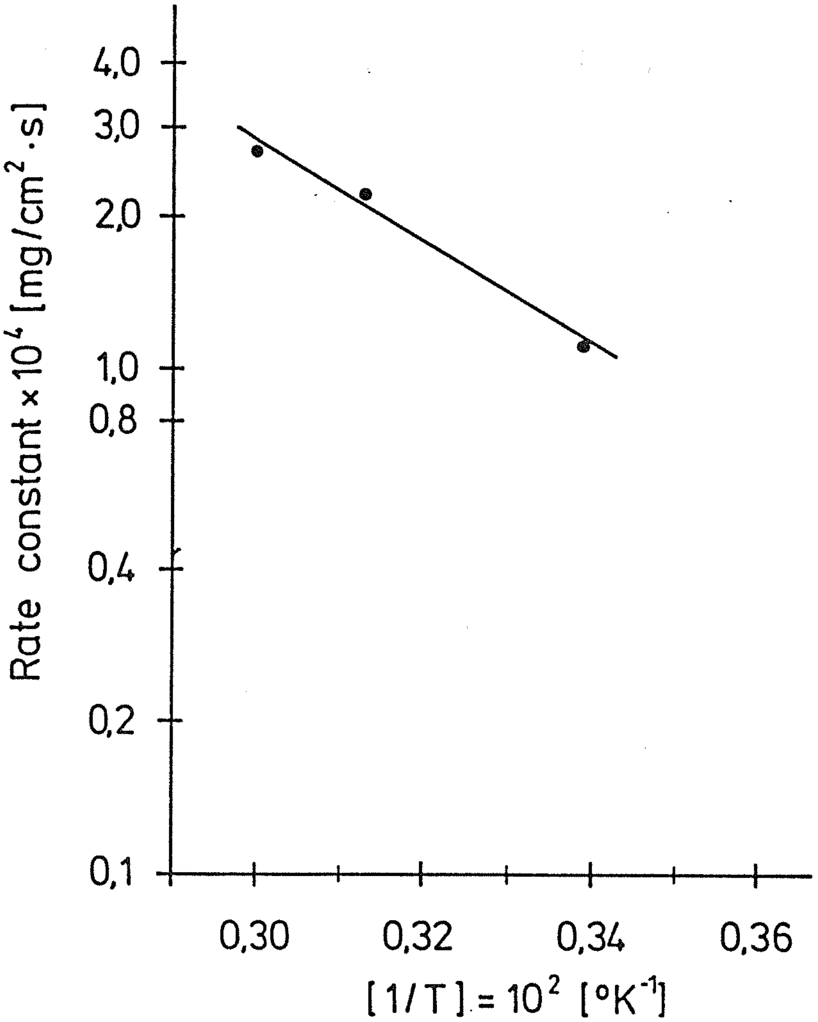

Fig. 10: Arhenius plot for the dissolution rate of iron (pH = 1.3)