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KINETIC STUDY OF BASIC ZIRCONIUM SULFATE PRECIPITATION

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A B S T R A C T

Hydrometallurgical treatment of $ZrCl_4$ for ZrO_2 producing involves the precipitation of basic zirconium sulfate ($Zr_5O_8(SO_4)_2 \cdot xH_2O$) according to the overall reaction:

$$5\ ZrCl_2 + 3H_2O + 2H_2SO_4 \rightarrow Zr_5O_8\ (SO_4)_2 + 10\ HCl$$

The major variables considered were temperatura and concentrations of zirconium oxychloride and sulfuric acid. Kinetics was investigated at temperatures from 50°C to 65°C.

Experiments were carried out in a double wall vat with a circulating water bath, in order to keep the desired temperatures constant. To follow the reaction various techiniques such as molecular absorption spectrophotometry and pH measurements were tried.

The proposed model is discussed in comparison with experimental data from pilot plant tests, using commercial zirconium chloride.

1. INTRODUCTION

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The hydrometallurgical treatment of zirconium chloride to produce ZrO_2 of very low iron content, involves precipitation of zirconium, from solution, as basic zirconium sulphate:

$Zr_5O_8(SO_4)_2$.

Previous studies about the matter had the aim of evaluating process possibilities, as far as the purity of ZrO_2 is concerned. Operational data are poor, with little care about rates. However, it was observed that, at least some concentrations parameters might be critical (1,2).

As the research work on a process for ZrO_2 production from caldasite was carried on, it has become more evident the need of a more fundamental approach. Also, the beginning of pilot plant scale tests have demanded a more detailed data which could make optmization procedures easier. The problems were still aggravated by the few thermodynamical measurements made on zirconium compounds.

This paper describes a kinetic study of the reaction between $ZrOCl_2$ and SO_4^{2-} to give $Zr_5O_8(SO_4)_2$.

2. EXPERIMENTAL TECHNIQUES

The *pH* measurements, which enabled to estimate the equilibrium constant for $ZrOCl_2$ hydrolisis reaction, were carried out in a double wall vessel with a circulating bath, to keep constant the desired temperatures.

A molecular absorption spectrophotometer, with a flow-through type cell, was used to

follow up the reaction sequence. Fig.1 shows, schematically, the procedure used.

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All chemical substances were supplied by Merck or Baker at the highest purity degree available.

The *pH* meter was a Beckman Expandomatic model SS-2 and the spectrophotometer was a Pye Unicam SP-1800 instrument.

3. $ZrOCl_2$ HYDROLISIS

There are some references about the hydrolisis of $ZrOCl_2$ solutions (3,4). Probably, the easiest way to detect the fact is through the *pH* variation which occurs in new prepared zirconil chloride solutions. However, changes in solution composition was also confirmed by measuring absorbance at a wave length of 200 nm.

There are some controversy about the ionic zirconium containing species existing in solutions and several possibilities have been mentioned (3). The kinetic study would possibly be much more difficult in the presence, of appreciable amounts of more than one ionic specie.

Investigation on the equilibrium constant concerned to the hydrolisis of the ZrO^{2+} specie was carried out in order to select the conditions to be used for the kinetic measurements.

Hydrolisis reaction may be schematized:

$$ZrO^{2+} + H_2O \rightarrow ZrOOH^{+} + H^{+}$$

If the above reaction is supposed to happen and activities factors are neglected, one will have:

$$K = \frac{(H^{+})\ (ZrOOH^{+})}{(ZrO^{2})}$$

Solutions used for experiments had a very low content of $ZrOCl_2$, compared to the other substances.

The reaction evolution was well described by the following rate equation:

$$d\ (ZrOCl_2) = (-K_1(ZrOCl_2) + K_2)\ dt$$

The supposition for the reverse reaction being of the zeroth order is not only reasonable, but has some experimental support.

Certainly $(ZrOCl_2)$, at a time t, is given by the relation:

$$(ZrOCl_2) = C_o - MA$$

where: A = absorbance at time t

C_o = initial concentration of

M = constant

At equilibrium:

$$-K_1\ (ZrOCl_2)_{eq} + K_2 = 0$$

or $$K_2 = K_1\ (ZrOCl_2)_{eq}$$

Solving the former differential equation and, taking into account the above relationships:

$$\frac{Aeq - A}{Aeq} = e^{-K_1 t}$$

where: $(ZrOCl_2)_{eq}$ = final concentration of $ZrOCl_2$

The conditions and the results from investigations at 50°C, 55°C, 60°C and 65°C can be seen in Table II and fig. 3. Temperature dependence and activation energy are shown in Fig. 4.

Two additional series of isothermal measurements were carried out for determining the influences of SO_4^{2-} e H^+ concentrations. Data are summarized in Tables III and IV and in Fig. 5.

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As can be seen easily:

$$A_{eq} = \frac{Co}{M} - \frac{K_2}{K_1 M}$$

And the value of K_2 could be calculated from the plot of A_{eq} versus Co.

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An experiment was run at 50°C resulting in a value of 1.4×10^{-5} mol/min for K_2. This value will surely result in a very low equilibrium concentration of $ZrOCl_2$ for the majority of practical conditions.

5. CONCLUSION

As a consequence from the experiments considered in the last section, it was found that $Zr_5O_8(SO_4)_2$ precipitation kinetics could be described by the equation:

$$\frac{d(ZrOCl_2)}{dt} = 7.74(SO_4)^{-2,5}(H^+)^{-1}(ZrOCl_2) mol/min \times e^{-\frac{55.600J}{RT}}$$

R = gas constant

T = temperature (K)

It is worth to keep in mind that any conditions, far from those chosen for the experiments may cause a deviation from the above description.

The final results have showed a good correlation with pilot plant tests. Thanks to that, it was possible an easier operation for the hydrometallurgical treatment of zirconium chloride.

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TABLE I

pH of $ZrOCl_2$ Solutions at Different Concentrations

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	pH	
	24°C	30°C
1.31×10^{-2}	2.09	2.12
6.55×10^{-3}	2.34	2.36
3.78×10^{-3}	2.61	2.61
2.62×10^{-3}	2.67	2.65
1.31×10^{-3}	2.90	2.88
Slope	2.2	2.0
K	2.3×10^{-3}	9.8×10^{-3}

TABLE II

Observed Values for K_1 at Several Temperatures

$C_o = 8.73 \times 10^{-4}$ M

$(K_2SO_4) = 6.67 \times 10^{-3}$ M

$(H\ ClO_4) = 1.59 \times 10^{-2}$ M

Temp (°C)	K_1 (min^{-1})
50	0.13
55	0.20
60	0.26
65	0.33

TABLE III

Variation of K_1 with Sulphate Concentration

$C_o = 8.73 \times 10^{-4}$ M

$(HClO_4) = 1.59 \times 10^{-2}$ M

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(SO_4^{2-})	K_1 (min^{-1})
6.67×10^{-3}	0.45
8.89×10^{-3}	0.28
1.11×10^{-2}	0.12
1.33×10^{-2}	0.091

TABLE IV

Variation of K_1 with Acid Concentration

$C_o = 8.73 \times 10^{-4}$ M

$(HClO_4) = 1.59 \times 10^{-2}$ M

$(HClO_4)$	K_1 (min^{-1})
1.59×10^{-2}	0.31
2.47×10^{-2}	0.20
2.91×10^{-2}	0.18
4.23×10^{-2}	0.11

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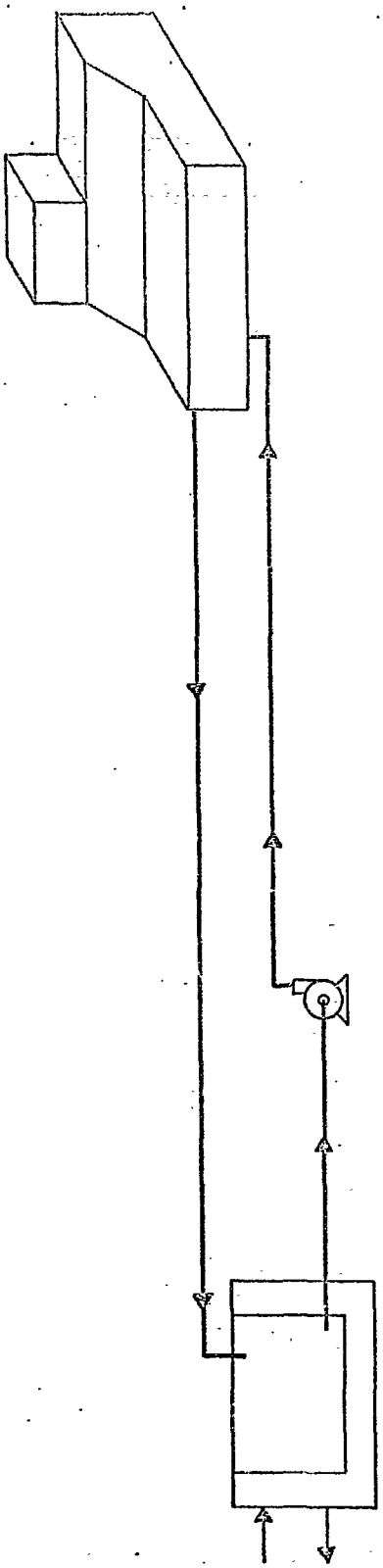

Fig_1

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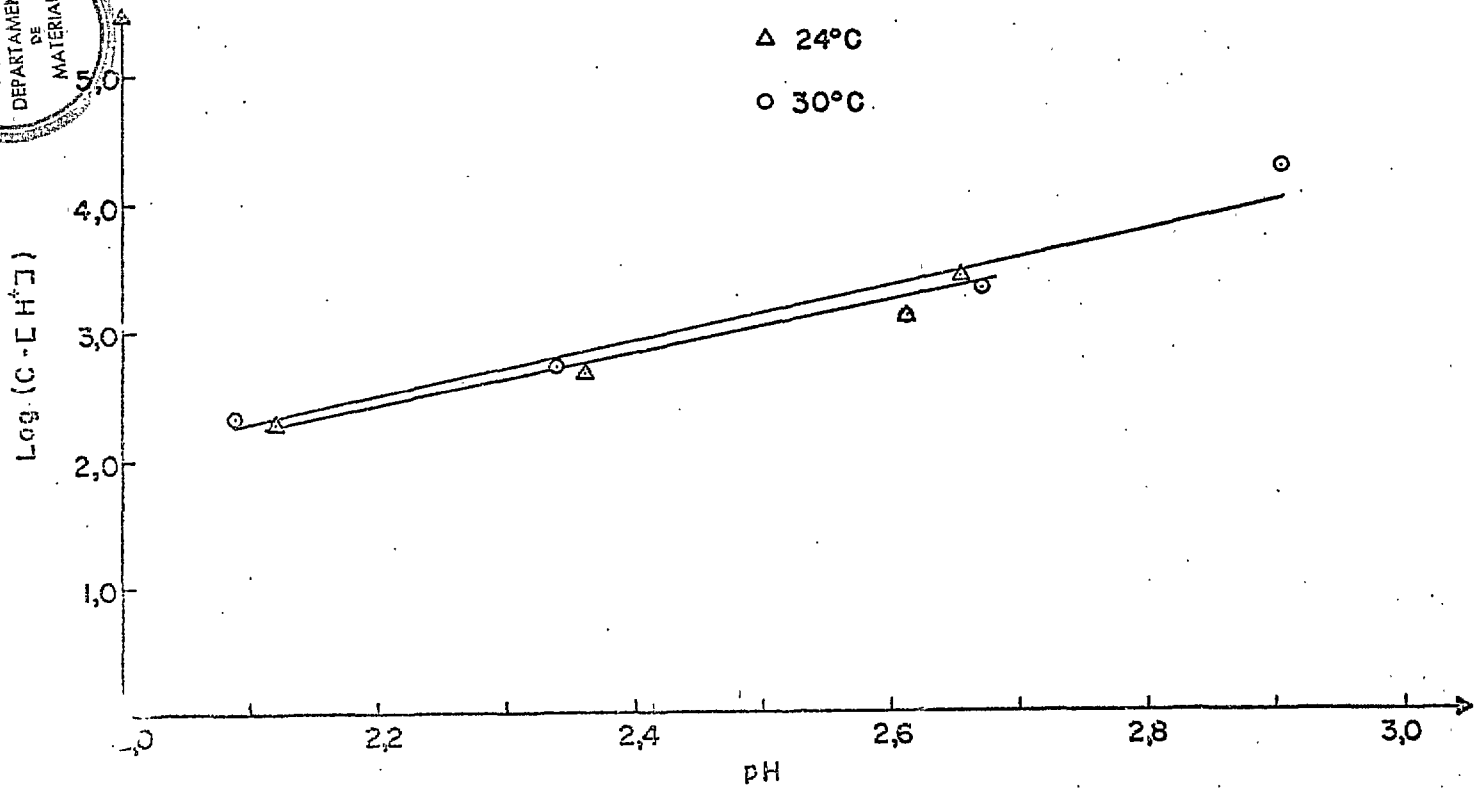

Fig_2

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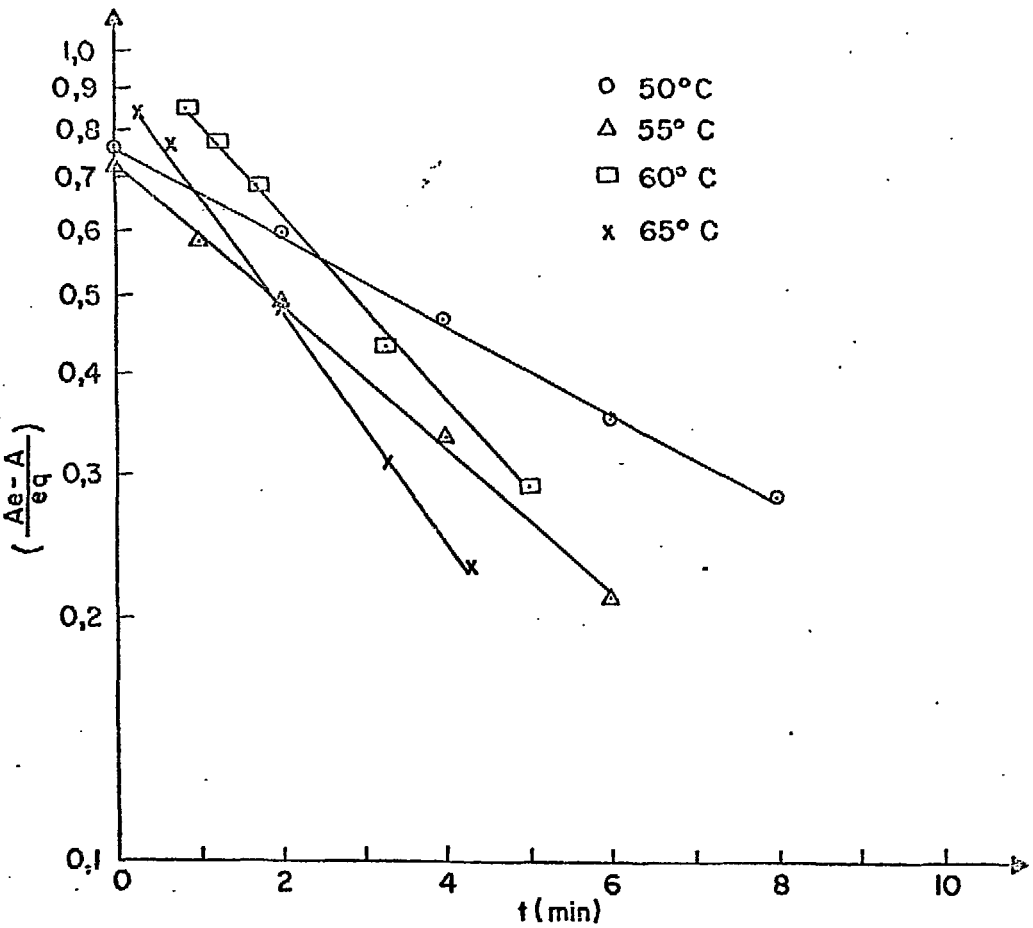

Fig_3

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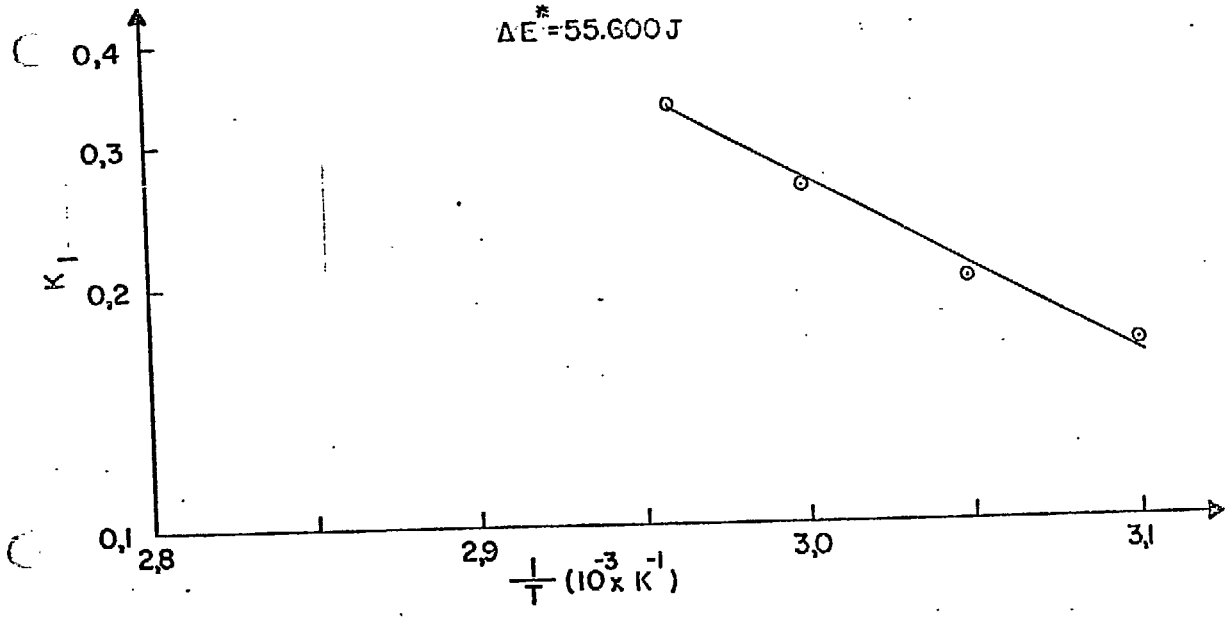

Fig_ 4

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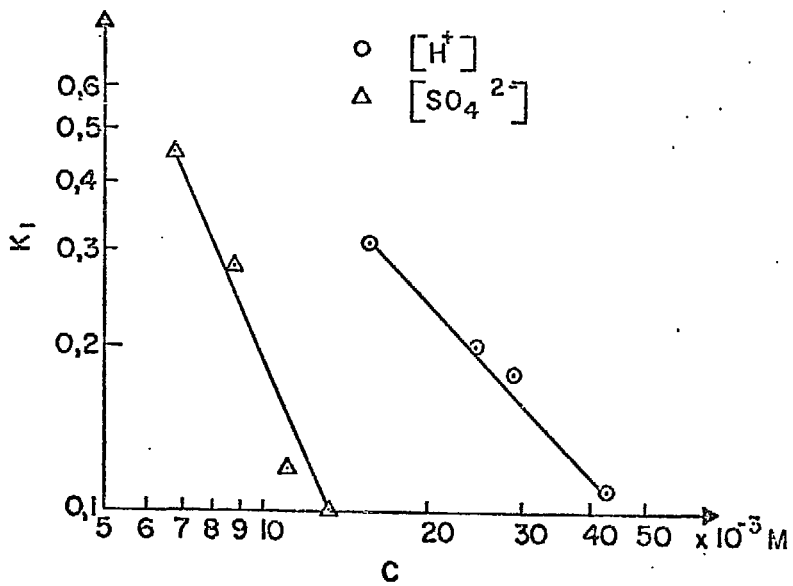

Fig_5