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TECHNICAL DIVISION  
SAVANNAH RIVER LABORATORY

DPST-80-358

ACC. NO. 142323

CC: J. A. Kelley  
R. M. Wallace  
L. R. Austin, 679-G  
R. B. Ferguson  
J. R. Wiley  
P. K. Baumgarten  
L. L. Kilpatrick  
D. A. Whitehurst, 679-G

MEMORANDUM

April 25, 1980

TO: J. K. OKESON

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FROM: L. P. MACINTYRE

STRONTIUM ION EXCHANGE RESIN EVALUATION

SUMMARY

Experiments were undertaken to characterize the two resins Lewatit\* TP-207 and Amberlite\*\* IRC-718, now under consideration for use in the DWPF for strontium ion exchange. The effect of strontium, sodium and anion concentration on distribution coefficient  $K_d$  between resin and idealized simulated DWPF supernate were required as basic data for the cesium/strontium tracer-level facility in Room C-139, Building 773-A. Affinity (selectivity) series data consisting of distribution coefficients  $K_d$  for the various other nuclides in solution were also needed. The affinity series available from the manufacturers were for lower pH than exist in the supernate. As analytical tools we used  $^{85}\text{Sr}$  tracer to determine strontium  $K_d$ 's and atomic absorption for nuclides other than strontium.

The two resins acted similarly, so that it was possible to draw general conclusions about their action:

- I. Strontium concentration has no effect on Sr  $K_d$ 's until the capacity of the resin (5-6 meq/g) is reached.
- II. Both resins are very specific to strontium in the absence of  $\text{CO}_3^{=}$  and  $\text{SO}_4^{=}$  i.e., the Sr  $K_d$  is higher than any other (see Table VI). The Sr  $K_d$  (on a dry weight basis) for the Amberlite is 3250, with the next ion in the affinity series, Hg, with  $K_d = 840$ . The Sr  $K_d$  for the

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Lewatit is 6930, with the next ion, Ca, with  $K_d = 1130$ . Sr  $K_d$ 's for Lewatit remain higher than those for Amberlite even with complexing anions  $\text{CO}_3^-$  and  $\text{SO}_4^-$  added to the solutions.

- III. The log of the Sr distribution coefficient  $K_d$  decreases linearly with the log of the sodium concentration. The slope of the lines was somewhat greater than the -2 predicted from resin-liquid equilibrium considerations.
- IV. The effect of  $\text{CO}_3^-$  and  $\text{SO}_4^-$  present in actual plant ion exchange feed was to reduce Sr  $K_d$  but not below the  $K_d$ 's of the competing cations. Increasing  $\text{OH}^-$  concentration also reduced Sr  $K_d$ . The  $\text{CO}_3^-$ ,  $\text{SO}_4^-$  and  $\text{OH}^-$  anions will probably have a similar effect on competing cations as on Sr, so that the cations should not interfere as much with Sr ion exchange as previously thought.

Tentatively, the Lewatit resin seems better for our use, due to its higher strontium  $K_d$ 's. Other factors, such as elution behavior, resin density, resistance to radiation, and dependability of supply (the Lewatit resin is manufactured in Germany) will also have to be considered.

## DISCUSSION

### Experimental

Prior to the experimental work, information was developed on the cations likely to be found in the waste supernate and apt to interfere with strontium in the ion exchange process. Reference 1 was used to determine the solubility at pH = 13 of  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Yb}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Sn}^{4+}$ ,  $\text{Nd}^{3+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Ru}^{2+}$ . Calculations were then made to decide on the proper concentration of the elements to be used for  $K_d$  measurements. This included determining the minimum concentration analyzable by atomic absorption and calculating the concentration necessary to measure  $K_d$ 's in the range of 100 to 10,000.

Solutions of those elements ( $\text{Ag}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Yb}^{2+}$ ) that would dissolve in the idealized supernate solution (1.0M NaOH - 4.75M  $\text{NaNO}_3$ ) in suitable concentrations were made up. Fifteen ml of each solution was placed in a small bottle along with 0.1g resin and shaken for 24 hours. Samples of the solution before and after contact with the resin, were analyzed by AA for the cation being tested.  $K_d$ 's were calculated using the formula:

$$K_d = \frac{15 \text{ ml}}{\text{dry wt of resin}} \frac{\text{feed concentration}}{\text{equilibrium solution concentration}} - 1$$

Although the resin was added wet, calculations were based on dry weight. To obtain the dry weight/wet weight ratio, samples of each resin were first weighed, then air dried and weighed again.

The same basis (15ml solution, 0.1g resin) was used to measure strontium  $K_d$ 's at various concentrations of  $\text{Sr}^{2+}$ ,  $\text{Na}^+$ ,  $\text{CO}_3^-$ , and  $\text{SO}_4^-$ . Strontium-85 tracer was used, rather than atomic absorption, to measure the strontium uptake of the resin. The solutions were counted with and without resin contact. Gamma counts were made using a sodium iodide detector. Since the solutions (with and without resin contact) were counted within minutes of each other, no compensation for decay was necessary.

Sr  $K_d$  vs.  $Sr^=$  Concentration

It can be shown from equilibrium considerations for the case of constant sodium concentration that

$$K_d^{1/2} = K_1^{1/2}C - 2K_1^{1/2}[Sr], \text{ where:}$$

K is equilibrium constant for  $Sr^{2+}$  uptake on the sodium form of the resin:

$$K = \frac{[Sr] [Na]^2}{[Sr] [Na]^2}$$

$$K_1 = \frac{K}{[Na]^2} = \frac{[Sr]}{[Sr] [Na]^2}$$

$[Na]$  = Sodium concentration on resin.

$[Na]$  = Sodium concentration in treated solution.

$[Sr]$  = Strontium concentration on the resin.

$[Sr]$  = Strontium concentration in treated solution.

C = Exchange capacity of resin.

$$K_d = \frac{[Sr]}{[Sr]}$$

Therefore,  $K_d^{1/2}$ , when graphed vs.  $[Sr]$ , should produce a straight line. Straight lines were obtained, as seen in Figure 1. Data can be found in Table I.

Sr  $K_d$  vs.  $Na^+$  Concentration

Similarly, for the case of dilute Sr concentration, where the Sr concentration on the resin is always small relative to the Na concentration on the resin:

$$\log K_d = \log K_2 - 2 \log [Na], \text{ where:}$$

$$K_2 = K[Na]^2$$

$K_d$  results were plotted on log-log paper as shown in Figure 2, and will also be found in Table II. Straight lines were obtained as predicted. The slopes of these lines were not -2, but -1.49 for the Lewatit, and -1.25 for the Amberlite. The equation is then changed to:

$$\log K_d = \log K_2 - m \log [Na^+] \text{ where:}$$

m = slope

Futher work needs to be done in order to explain why the slopes differed from a value of 2.

Sr  $K_d$  vs. Anion Concentration

The competition between anions and the resin for the strontium must also be considered. Here the defining equation (also for dilute Sr concentration) is as follows:

$$\frac{1}{K_d} = \frac{1}{K_d^0} + \frac{K_e}{K_d^0} [A], \text{ where:}$$

[A] is the anion concentration in the solution.

$K_d^0$  is the  $K_d$  with no anion present.

$K_e$  is the equilibrium constant for the anion complex.

$$K_e = \frac{[SrA]}{[Sr] [A]}$$

This equation should define the behavior of the anions tested,  $OH^-$ ,  $CO_3^{2-}$ , and  $SO_4^{2-}$ . For  $OH^-$  and  $CO_3^{2-}$ , the graph agrees with theory (see Figures 3 and Tables III and IV). For  $SO_4^{2-}$ , there is deviation below 0.1M concentration (see Figure 5 and Table V). Further work is necessary in this region to ascertain the cause of this effect.

Affinity Series

Affinity series data for strontium and competing ions for the idealized supernate are shown in Table VI. Both resins are highly specific for strontium. The Lewatit resin outperformed the Amberlite resin both with and without added anions. The  $K_d$  of the Lewatit resin for strontium is over three times that of the Amberlite resin. The nearest competitor on Amberlite resin is mercury with a  $K_d$  about one-quarter that of strontium. The nearest competitor on Lewatit resin is calcium with a  $K_d$  about one-sixth that of strontium. A work of caution is necessary since the overall ion exchange process also depends on  $K_d$ 's in the presence of the elutriant (0.01M  $Na_4$  EDTA). If the Lewatit resin cannot be eluted easily, it would then be unsatisfactory. Also, the Lewatit resin is somewhat less dense than the Amberlite resin, so that on a volume basis the Lewatit  $K_d$ 's are somewhat less relatively than indicated. Although strontium is complexed by  $CO_3^{2-}$  and  $SO_4^{2-}$  anions, the likelihood is that competing cations are similarly complexed, so that both resins will still be selective to strontium.

The resin capacity will probably not be the limiting factor on number of column volumes throughput. Rohm and Haas lists a cation exchange capacity of 5.3 meq/g dry resin  $\approx$  1.1 meq/ml wet resin for Amberlite IRC-718. Based on an estimated  $5 \times 10^{-3}$  N concentration of all the competing cations in the ion exchange feed, the resin could handle as much as 200 column volumes of feed, as compared to the flowsheeted 40 column volumes. This is a conservative estimate since mercury is present in high concentration but is likely to exist in anion rather than cation form. Individual ions are believed to be sorbed or exchanged separately, so that they should not interfere with each other as long as the exchange capacity is not approached. The future tracer-level column tests and the high-level cell tests with actual dissolved salt and supernate will furnish additional information on these questions.

REFERENCES

1. Kragten, J. Atlas of Metal-Ligand Equilibria in Aqueous Solution. Sussex:  
Ellis Horwood, Ltd., 1978.

TABLE I

RESIN EQUILIBRIUM DATA FOR VARYING Sr CONCENTRATION

	<u>Sr<sup>2+</sup> Concentration in Feed Solution</u>	<u>K<sub>d</sub></u>	<u>Sr<sup>2+</sup> Concentration on Resin</u>
	M	<u>meq/g dry resin meq/ml liquid</u>	<u>millimols g</u>
Amberlite	10 <sup>-2</sup>	1810	0.92
	10 <sup>-3</sup>	3223	0.36
	10 <sup>-4</sup>	3121	0.03
	10 <sup>-11</sup>	3400	0.00
Lewatit	10 <sup>-2</sup>	2298	0.98
	10 <sup>-3</sup>	6386	0.24
	10 <sup>-4</sup>	7305	0.03
	10 <sup>-11</sup>	7111	0.00

TABLE II

RESIN EQUILIBRIUM DATA FOR VARYING Na CONCENTRATIONS

<u>Na Concentration in Solution</u>	<u>Amberlite K<sub>d</sub></u>	<u>Lewatit K<sub>d</sub></u>
M	<u>meq/g dry resin meq/ml liquid</u>	<u>meq/g dry resin meq/ml liquid</u>
1	21607	81911
2	9210	26918
3	5211	15112
4	3710	10376
5	2866	7291

TABLE III

RESIN EQUILIBRIUM DATA FOR VARYING OH CONCENTRATIONS

<u>OH Concentration in Solution</u>	<u>Amberlite K<sub>d</sub></u>	<u>Lewatit K<sub>d</sub></u>
M	<u>meq/g dry resin meq/ml liquid</u>	<u>meq/g dry resin meq/ml liquid</u>
0.1	2801	15504
0.5	2544	5784
1.0	3121	7305
2.0	1205	2796
4.0	619	1194
5.75	390	591

TABLE IV

RESIN EQUILIBRIUM DATA FOR VARYING CO<sub>3</sub> CONCENTRATIONS

<u>CO<sub>3</sub><sup>2-</sup> Concentration in Solution</u>	<u>Amberlite K<sub>d</sub></u>	<u>Lewatit K<sub>d</sub></u>
M	<u>meq/g dry resin meq/ml liquid</u>	<u>meq/g dry resin meq/ml liquid</u>
0.1	2436	3495
0.2	1418	2818
0.3	1040	1972
0.4	815	1695

TABLE V

RESIN EQUILIBRIUM DATA FOR VARYING SO<sub>4</sub> CONCENTRATIONS

<u>SO<sub>4</sub><sup>2-</sup> Concentration in Solution</u>	<u>Amberlite K<sub>d</sub></u>	<u>Lewatit K<sub>d</sub></u>
M	<u>meq/g dry resin meq/ml liquid</u>	<u>meq/g dry resin meq/ml liquid</u>
0.1	2554	4145
0.2	2431	4033
0.3	2358	3916

TABLE VI

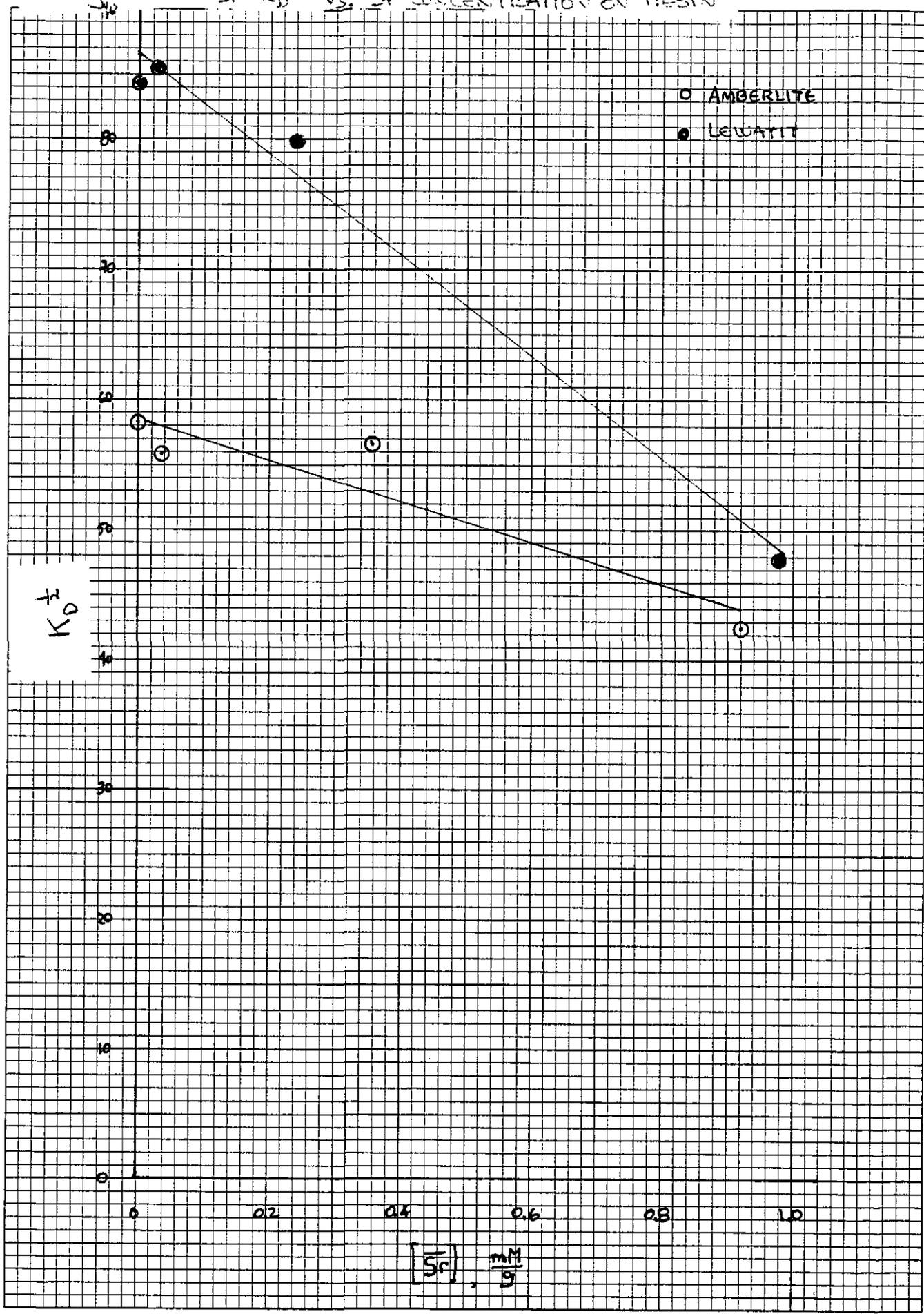
AFFINITY SERIES FOR AMBERLITE IRC-718 AND LEWATIT TP-207  
IN 1.0M NaOH - 4.75M NaNO<sub>3</sub>

Amberlite					
Ion*	K <sub>d</sub>		Ion*	K <sub>d</sub>	
	Feed Concentration, ppm	<u>meq/g dry resin</u> <u>meq/ml liquid</u>		Feed Concentration ppm	<u>meq/g dry resin</u> <u>meq/ml liquid</u>
Sr	**	3248	Sr	**	6934
Hg	31	840	Ca	15	1130
Yb	49	674	Ba	54	690
Ca	15	293	Cu	59	618
Ba	54	176	Yb	49	525
Ag	29	89	Hg	31	365
Cr	41	53	Ag	29	233
Cu	59	38	Cr	41	38
Pb	230	28	Pb	230	6

\*All added as nitrates except strontium which was added as SrCl<sub>2</sub> tracer solution plus natural Sr(NO<sub>3</sub>)<sub>2</sub>.

\*\*Average of data for 10<sup>-11</sup> to 10<sup>-3</sup> molar Sr<sup>2+</sup> (5 x 10<sup>-6</sup> ppm to 80 ppm).

Figure 1. Sr  $K_D^{\frac{1}{2}}$  vs. Sr CONCENTRATION ON RESIN



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Figure 2. SR K<sub>o</sub> vs. Na CONCENTRATION IN SOLUTION

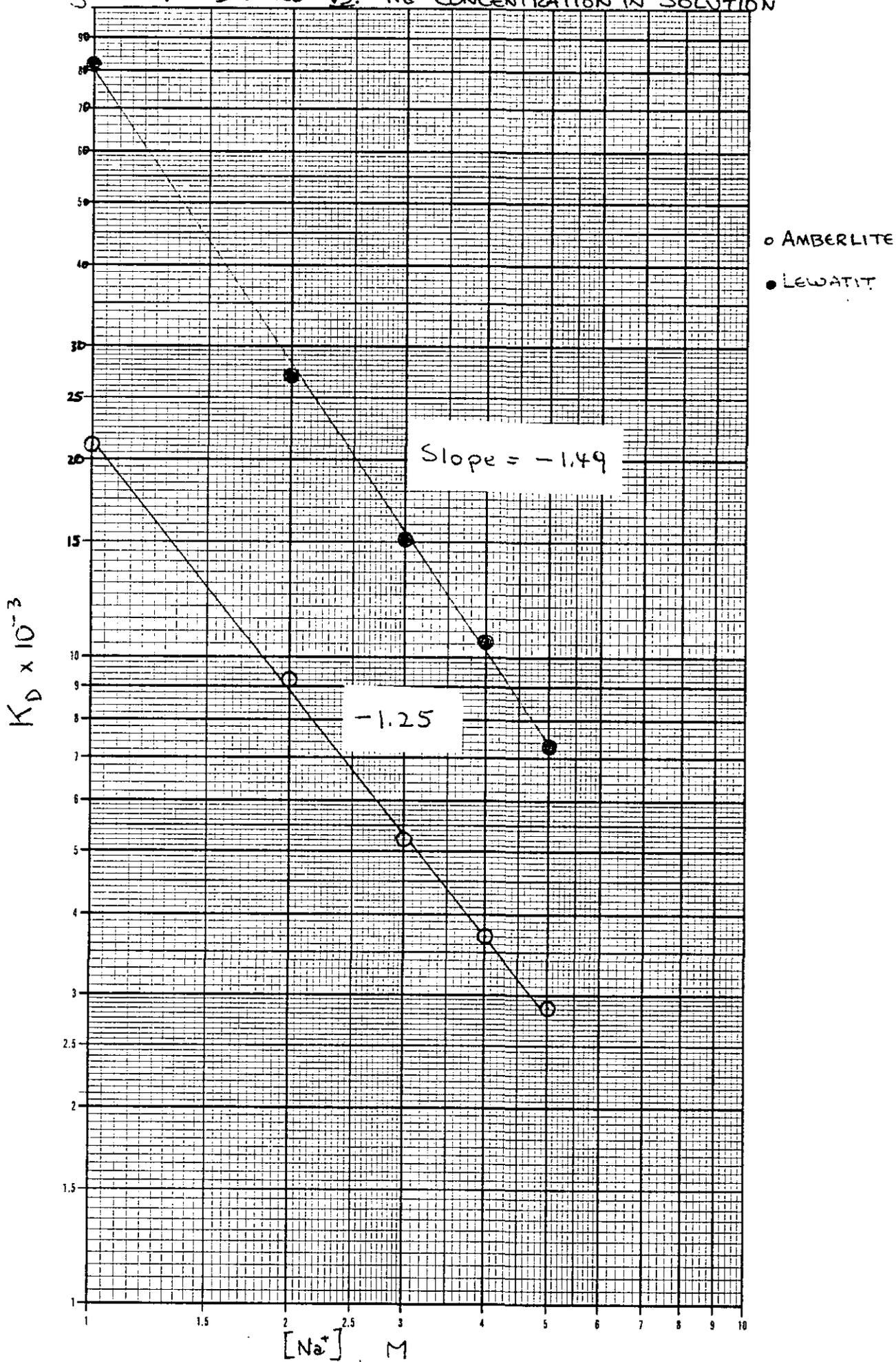
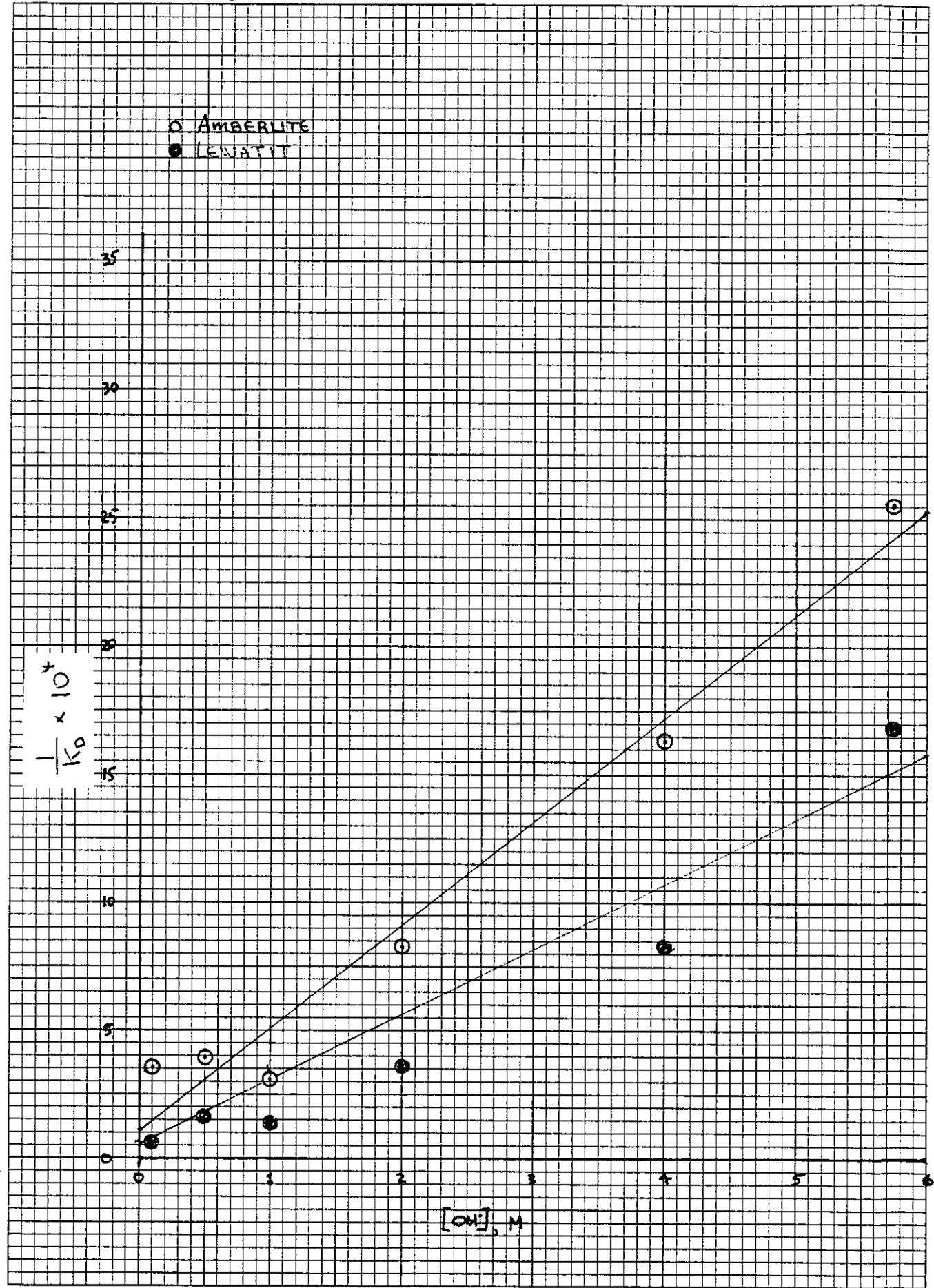


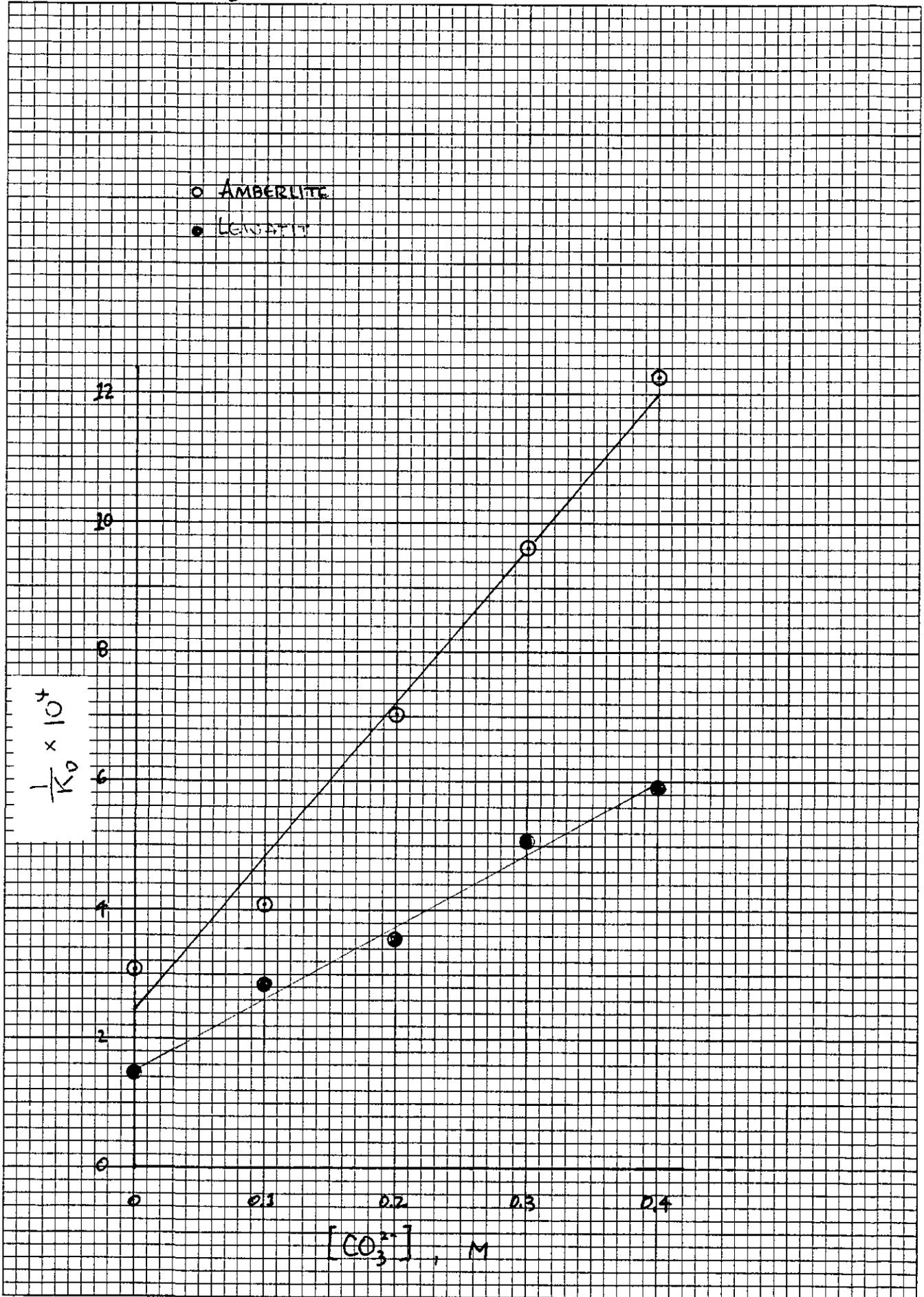
Figure 3.  $\frac{1}{Sr K_D}$  vs. OH CONCENTRATION IN SOLUTION



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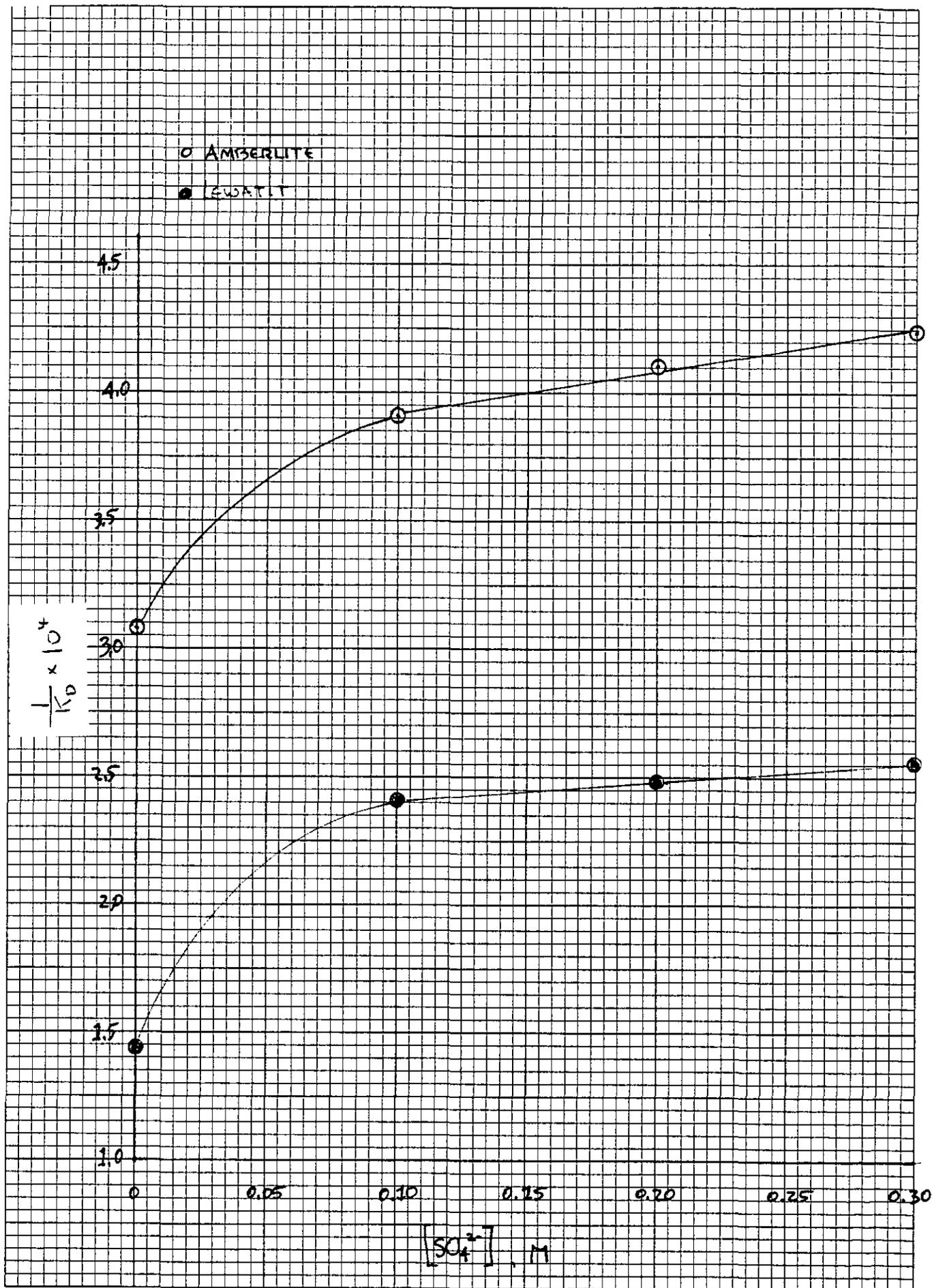
Figure 4,  $\frac{1}{S r K_D}$  vs.  $CO_3$  CONCENTRATION IN SOLUTION



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Figure 5.  $\frac{1}{Sr K_D}$  vs.  $SO_4$  CONCENTRATION IN SOLUTION



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