

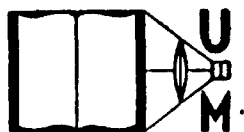
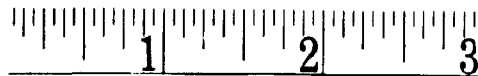
DOCTORAL DISSERTATION SERIES

TITLE *The Colloidal State And Precipitation Of
Certain Metallic Hydroxides In Concentrated
Solutions Of Nickel Sulfate*

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THE COLLOIDAL STATE AND PRECIPITATION OF CERTAIN METALLIC HYDROXIDES IN CONCENTRATED SOLUTIONS OF NICKEL SULFATE

A study has been made of the factors effecting the formation of the hydroxides of aluminum, cadmium, trivalent and hexavalent chromium, cupric copper, ferrous and ferric iron, and zinc in strong solutions of nickel sulfate, boric acid and buffered nickel sulfate with the object of determining the pH values at which the hydroxides began to precipitate, and at which they were completely removed from solution.

Various pH studies of precipitation of metallic hydroxides have been reported in the literature but the only previous extensive investigations similar to the present one are those of Hildebrand (1) and of Britton (2).

Atkins (3) found colorimetrically that ferrous hydroxide precipitated from ferrous sulfate solutions between pH 5.1 and 7.6, while Patten and Mains (4) found the range to be more specifically between pH 5.5 and 6.0. Pickering (5) observed that complete precipitation of ferrous iron had occurred at the pH where the solution was alkaline to phenolphthalein.

Hiller (6) investigated the composition of the precipitates formed from alum solutions upon addition of alkali. A pH of 5.5 (colorimetric) was given as the value at which the precipitation of aluminum approaches completion. Blum (7) studied the precipitation of aluminum as oxide and from observations made with an hydro-

gen electrode and suitable indicators, for example, methyl red, found that the precipitation of aluminum hydroxide from aluminum chloride solutions was complete when H^+ was $10^{-6.5}$ to $10^{-7.5}$. Joffe and McLean (8) found that in the presence of sulfate-ions the aluminum from a .0075 M. solution was transformed completely into the gel at pH 4.7 to 4.8. However, in the presence of chloride-ion complete aluminum precipitation occurred at pH 5.4. Pridesux and Henness (9) in studying the precipitation of hydrous aluminum oxide reported visible precipitation from the sulfate solution at about pH 4, but not until about pH 6.5 in chloride solution.

While there is little agreement as to the exact pH values at which aluminum hydroxide starts to precipitate or at which it is removed from solution, the above investigations are in agreement that precipitation from sulfate solution occurs at a lower pH than from the chloride. This supports the general rule that the bivalent sulfate ion has a greater coagulating effect upon positive colloid than does the monovalent chloride ion.

Hildebrand and Bowers (10) found that zinc was removed at a pH of about 6.3. Kolthoff and Kameda (11) in their studies of the hydrolysis of zinc sulfate titrated various molar concentrations of zinc with sodium hydroxide. They obtained pH values of 6.17 and 6.49 at which zinc starts to precipitate from .05M and .01M zinc sulfate solutions, respectively. Britton (2) reported a pH

Experimental

Materials and Apparatus:- A stock solution of nickel sulfate was prepared by dissolving 2270 g. of Baker's Analyzed C.P. $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in 8 liters of distilled water. This solution was divided into two portions; one was treated with ammonium hydroxide, the other with sodium hydroxide solution, approximately .5N, until the pH was 6.7 to 6.8. The solutions were heated for one hour at 90°C , allowed to stand twenty-four hours, then filtered.

The metals were added in the form of their sulfates, except in the case of hexavalent chromium to give a metal content of approximately .5g./l. Baker's Analyzed Chemicals were used for aluminum, cadmium, iron and nickel sulfates. The $\text{Cr}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and CrO_3 were C.P. grades. The sulfates of copper and zinc were prepared from the pure metals. Boric acid was Baker's C.P. grade, and was recrystallized from water.

Analyses for cadmium, copper, and zinc were made employing a Leeds and Northrup Electro-Chemograph.

Measurements of pH were made with a laboratory model (G) Beckman pH meter.

Method of Analysis:- For the polarographic determination of cadmium and copper, the nickel sulfate solution served as a supporting electrolyte, but since the zinc and nickel waves come at approximately the same half-wave potential in the sulfate solution the zinc was

first separated from the nickel by the method of Fales and Ware (19), the sulfide was dissolved in cold 1:1 hydrochloric acid, evaporated to dryness, taken up in 25 ml. of a solution .1N ammonium acetate and .025N potassium thiocyanate, as suggested by Reed and Cummings (20).

Aluminum was determined by use of aurin tricarboxylic acid (26).

Chromium and iron were determined volumetrically using .05 and .01N potassium dichromate with diphenylamine sodium sulfonate as indicator. Trivalent chromium was oxidized to the hexavalent state with ammonium persulfate, then the above mentioned procedure followed.

Ferric iron was precipitated from the nickel sulfate solution by use of an excess of ammonium hydroxide, filtered, dissolved in warm 1:1 hydrochloric acid and the Zimmerman-Reinhardt method of analysis used. Ferrous iron was first oxidized to the ferric state with hydrogen peroxide, then the hydroxide precipitated with ammonium hydroxide.

Experimental Procedure:- Five hundred ml. of the purified nickel sulfate solution was acidified to a pH of 2.0-3.0 by addition of sulfuric acid solution. The weighed quantity of metallic salt was dissolved in the solution, then three 25 ml. samples were withdrawn for analysis. Ammonium hydroxide (1:4) was added dropwise while the solution was being stirred vigorously by means of a motor driven stirrer. A period of five minutes of

stirring was allowed after the NH_4OH additions before sampling. At 0.1-0.2 pH intervals two 25 ml. samples were withdrawn and pipetted into 7"x 5/8" test tubes. One series of samples was allowed to stand at room temperature (25°-27°C) for 24 hours with occasional shaking, while the other was heated in a boiling water bath for three hours. The test tubes in this second series were fitted with air condensers in order to minimize evaporation. These were made by almost closing off in a flame one end of a six inch piece of seven mm. tubing.

At the end of these periods observations were made as to the condition of the solutions, the samples filtered through No. 40 or 42 Whatman paper when the nature of the precipitate permitted, and pH measurements again made. Analyses were run on the solutions in the manner described earlier in the thesis.

The above procedure was repeated using 0.2N sodium hydroxide to raise the pH. Each metal was treated in the manner previously described with the exception of ferrous iron in which case it was necessary to keep an inert atmosphere above the solution and samples at all times during the run in order to prevent oxidation.

In the boric acid and buffered nickel sulfate series the solutions contained 37.5 g./l. of boric acid.

A nickel sulfate solution containing the following metals - aluminum, cadmium, copper, iron, magnesium, and

zinc in concentrations of 0.5 g./l. was treated with sodium hydroxide and procedure already described followed. The analyses were made spectrographically. The run was repeated using ammonium hydroxide.

Nickel carbonate and calcium hydroxide were added to buffered and unbuffered nickel sulfate solutions in order to determine the maximum pH values that could be obtained when the samples were thoroughly agitated at 25°C and when heated for 3 hours at 100°C.

Data and Discussion of Results

In the course of this investigation the question of obtaining the equilibrium pH values arose, since during precipitation hydroxyl ions were being removed from solution, thus changing the pH. This precipitation reaction sometimes required considerable time. Accordingly, it was decided that after each addition of base five minutes be allowed for stirring before the samples were collected and their pH determined. The pH's of these samples were again measured after standing 24 hours at room temperature (22-23°C) in order to obtain the equilibrium values. Measurements of pH were also made after the second series was heated 3 hours at 100°C. These data are recorded in the tables.

From a practical standpoint the pH value to which the solution must be raised in order to remove a certain amount of impurity would be most useful. The equilibrium

pH values do not always give this information since they are usually from 0.2-0.5 pH units lower than the initial values. Thus, in plotting the graphs the initial values were recorded.

Aluminum:- Initial appearance of turbidity upon addition of either ammonium or sodium hydroxide to buffered or unbuffered nickel sulfate solution containing aluminum sulfate was observed at $\text{pH } 4.4 \pm 0.1$ although buffer action was encountered at $\text{pH } 4.0$. The solutions rapidly became very turbid upon further addition of base and at $\text{pH } 4.6-4.7$ coagulation of the hydrous aluminum oxide was noted. As seen from Tables I (c) and (d) the concentration of the aluminum was markedly reduced at $\text{pH } 4.4$ upon standing for 24 hours. Heating the samples produced heavy precipitation at 0.3-0.4 pH units lower; however, the aluminum was not completely removed at $\text{pH } 4.9$. It may also be observed that in the case of the heated samples a considerable drop in the pH occurred even where no visible precipitation was in evidence, indicating hydrolysis had taken place.

Some difficulty was encountered in the use of aurintricarboxylic acid for low concentrations of aluminum. In order to have sufficient aluminum (0.1-0.5mg.) for the analysis 20ml. samples were taken. The high nickel sulfate content caused coagulation and settling of the lake so that it was necessary to shake the colorimeter tubes frequently while making check readings.

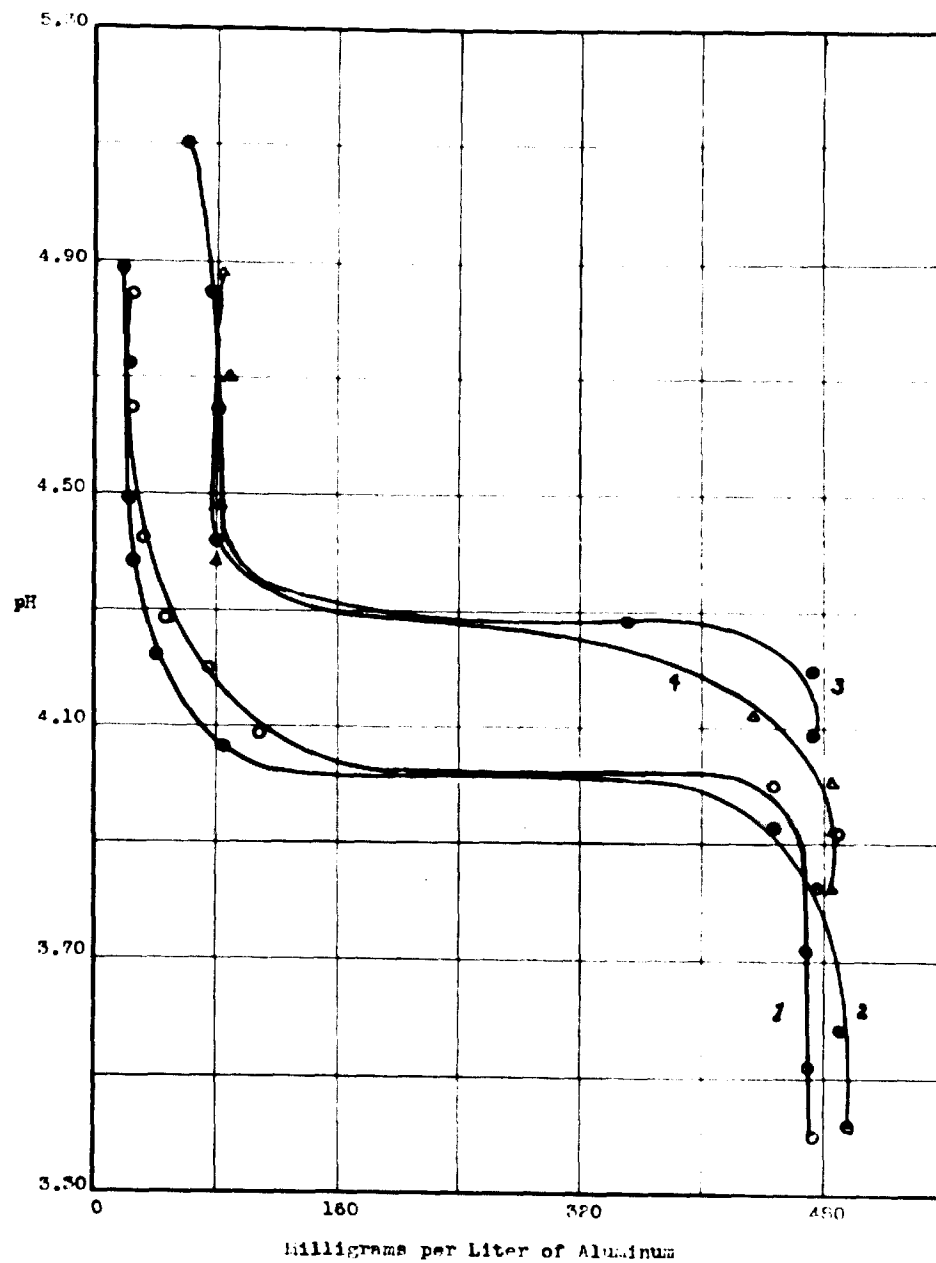


Fig. 1 - Aluminum in buffered nickel sulfate solution at different pH values: 1, NaOH treatment, 3 hrs at 100°C.; 2, NH₄OH treatment, 3 hrs at 100°C.; 3, NaOH treatment, 24 hrs at 25°C.; 4, NH₄OH treatment, 24 hrs at 25°C.

Removal of Aluminum from Nickel Sulfate Solution

Table I (a)

pH after addition of NH_4OH	Treatment	pH after treatment	Mg/l Al in soln
(orig soln)	none	-	500
	24 hrs		
4.18	at 25°C	4.18	458
4.29	"	4.25	458
4.54	"	4.46	265
5.02	"	4.67	18
	3 hrs		
3.80	at 100°C	3.08	500
3.89	"	3.08	500
4.02	"	3.13	480
4.18	"	3.03	350
4.40	"	2.61	41
5.02	"	2.74	17

Removal of Aluminum from Buffered Nickel Sulfate Solution

Table I (b)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l Al in soln
(orig soln)	none	-	485
	24 hrs		
3.83	at 25°C	3.85	485
3.93	"	3.93	485
4.01	"	4.05	485
4.12	"	4.13	431
4.38	"	4.32	79
4.49	"	4.45	83
4.72	"	4.72	90
4.88	"	4.84	86
	3 hrs		
3.42	at 100°C	3.13	492
3.58	"	3.14	487
3.83	"	3.18	476
3.93	"	3.18	445
4.07	"	2.75	89
4.22	"	2.51	38
4.38	"	2.62	25
4.49	"	2.71	21
4.72	"	2.82	20
4.88	"	2.88	19

Removal of Aluminum from
Buffered Nickel Sulfate Solution

Table I (c)

pH after addition of of NaOH	Treatment	pH after treatment	mg/l. Al in soln
(orig soln)	none	-	472
	24 hrs		
3.91	at 25°C	3.89	-
4.00	"	3.98	472
4.09	"	4.06	472
4.20	"	4.11	472
4.28	"	4.22	350
4.42	"	4.37	72
4.65	"	4.65	79
4.85	"	4.86	75
5.10	"	5.08	60
	3 hrs		
	at 100°C		
3.52	"	3.12	470
3.72	"	3.19	473
3.87	"	3.18	413?
3.92	"	3.17	488
4.00	"	3.13	415
4.09	"	2.94	107
4.20	"	2.62	77
4.28	"	2.57	44
4.42	"	2.62	30
4.65	"	2.75	24
4.85	"	2.80	24

Summary of Data on Aluminum

Table I (e)

Appearance of Turbidity

Solution	After addition of base		After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	4.4-4.6	4.4-4.5	4.3-4.4	4.3-4.4	?	3.8-3.9
Buffered NiSO ₄	4.4-4.5	4.3-4.4	4.05-4.15	4.0-4.1	3.8-3.9	3.9-4.0

Heavy Precipitation

Solution	After addition of base		After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	above pH 4.5	above pH 4.5	above pH 4.5	above pH 4.4	above pH 4.3	above pH 4.3
Buffered NiSO ₄	above pH 4.5	above pH 4.5	above pH 4.3	above pH 4.4	above pH 4.0	above pH 4.1

Removal of Aluminum

Solution	After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	trace at pH 4.9	trace at pH 5.06 trace at pH 5.37	trace at pH 4.9	trace at pH 4.63 abs. at pH 5.06
Buffered NiSO ₄	78mg/l remain pH 4.4 60 mg/l remain pH 5.1	86 mg/l remain pH 4.9	80 mg/l remain pH 4.4 24 mg/l remain pH 4.85	25 mg/l remain pH 4.4 19 mg/l remain pH 4.88

Cadmium:- Cadmium was not appreciably removed from a nickel sulfate solution with ammonium hydroxide up to a pH of 7.0, even upon heating for 3 hrs at 100°C. Above pH 7.2 - 7.5 there was some removed (see Table II (a)), but at the same time the nickel content of the solution was greatly reduced, so that the cadmium may have been carried down with the nickel hydroxide.

Sodium hydroxide was not used as a precipitant in this case since such a large volume of hydroxide solution would have been required to attain the desired pH values that the concentration of the cadmium would have been greatly lowered merely by dilution.

Similarly, in the case of buffered nickel sulfate solutions a number of precipitation studies were carried out using only ammonium hydroxide since the volume of dilute sodium hydroxide required to titrate the boric acid would have introduced a considerable dilution factor.

The importance of the metal concentration upon the pH at which precipitation occurs is brought out in Table II (g). It will be noted that in a boric acid solution with a cadmium content of 500 mg./l. no precipitation occurred up to a pH of 7.1 upon addition of ammonium hydroxide, and at the end of 24 hours at 25°C there was only a very faint turbidity at the same pH, whereas, with a solution, the original cadmium content of which was 1400 mg./l., precipitation started between pH 6.7 and 6.8.

Noteworthy also are differences in Tables II (a), (c) and (f). In the case of the heated samples there was very little precipitation of cadmium from nickel sulfate below pH 7, whereas in the boric acid solution heavy precipitation started between pH 6.0 and 6.3 and the cadmium concentration was reduced to approximately 40 mg./l. at pH 7. In a buffered nickel sulfate solution the cadmium was reduced only by 50 mg./l. at pH 6.87 after 3 hours at 100°C.

While making the run with cadmium in buffered nickel sulfate solution it was observed that between pH 6.2 and 6.3 the solution became very turbid and above 6.3 a large quantity of $\text{Ni}(\text{OH})_2$ was precipitated. This was about 0.6 pH unit lower than the value at which nickel hydroxide started to precipitate in an unbuffered solution. A run was then made in which the pH of a buffered nickel sulfate solution was raised with ammonium hydroxide. The results are shown in Table II (h) and in Fig. 2A.

In view of the heavy precipitation of nickel hydroxide above pH 6.3, the removal of cadmium from the buffered nickel sulfate solution cannot be attributed to the influence of the boric acid since it is entirely probable that some of the cadmium was adsorbed from solution by the nickel hydroxide,

It is evident also that any visual observation as to the pH values at which metallic hydroxides come down

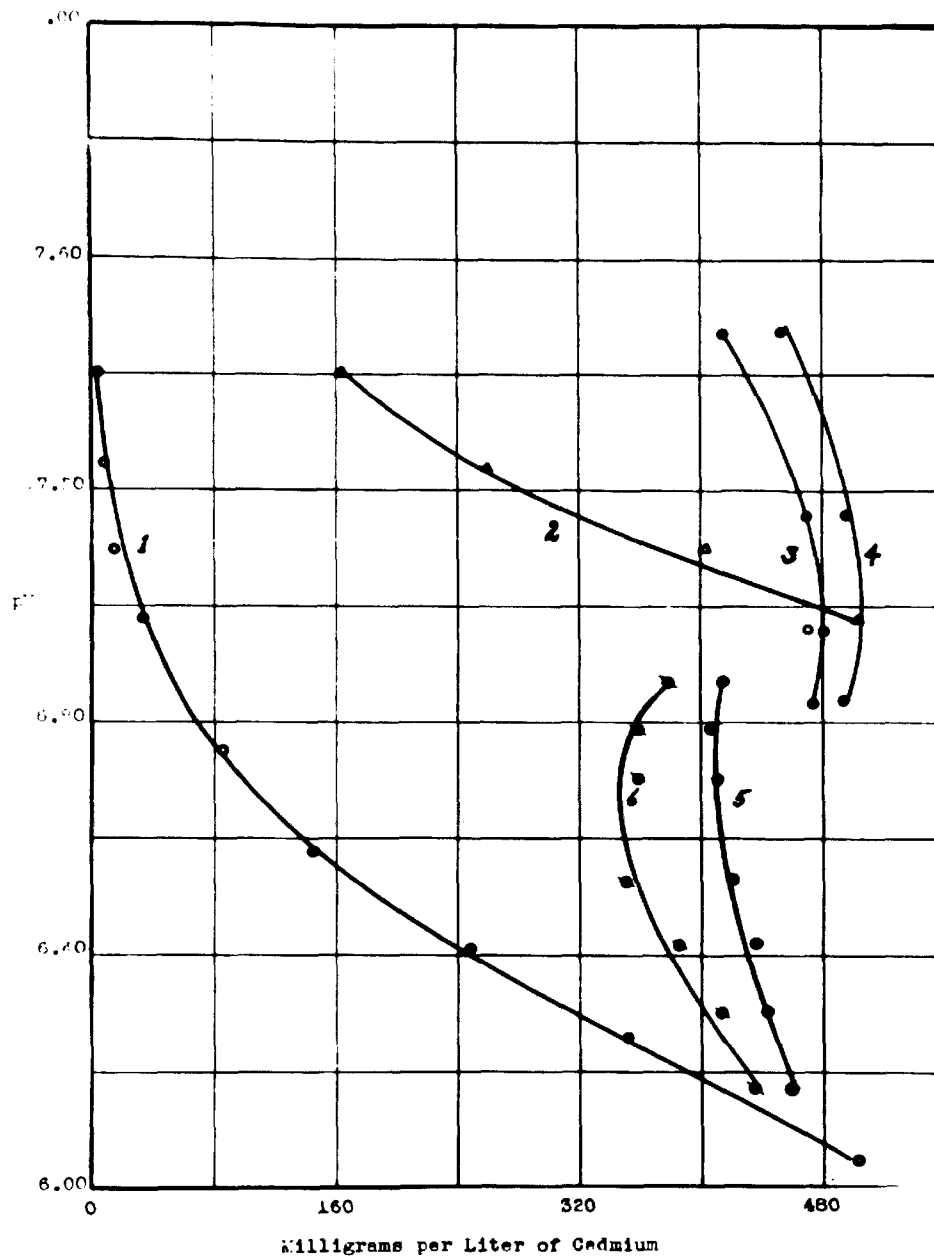


Fig. 2 - Cadmium in boric acid, nickel sulfate, and buffered nickel sulfate solutions at different pH values: 1, boric acid solution after NH_4OH treatment, 3 hrs at 100°C .; 2, boric acid solution after NH_4OH treatment, 24 hrs at 24°C .; 3, Nickel sulfate solution after NH_4OH treatment, 3 hrs at 100°C .; 4, Nickel sulfate solution after NH_4OH treatment, 24 hrs at 27°C .; 5, Buffered nickel sulfate solution after NH_4OH treatment, 3 hrs at 100°C .; 6, buffered nickel sulfate solution after NH_4OH treatment, 24 hrs at 24°C .;

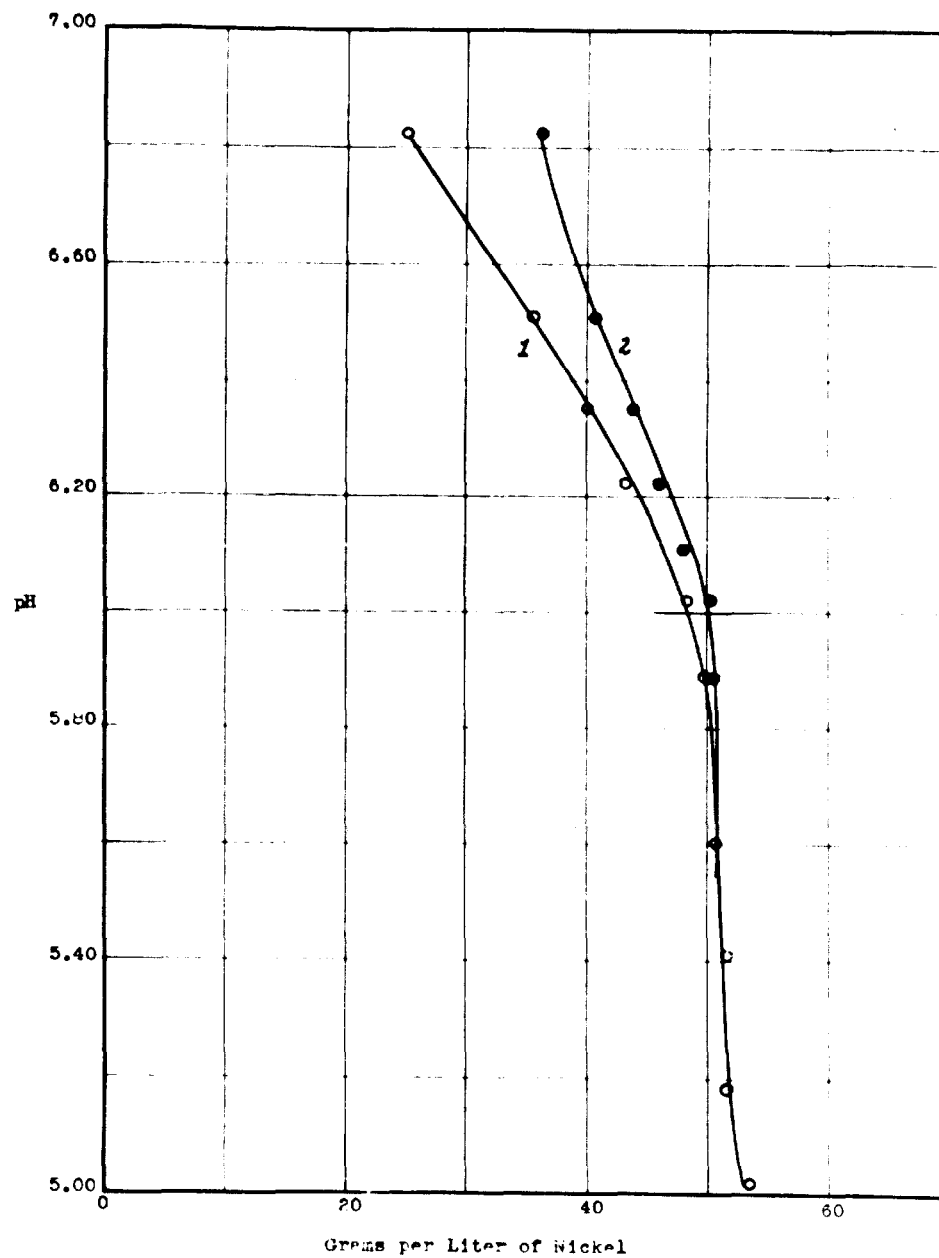
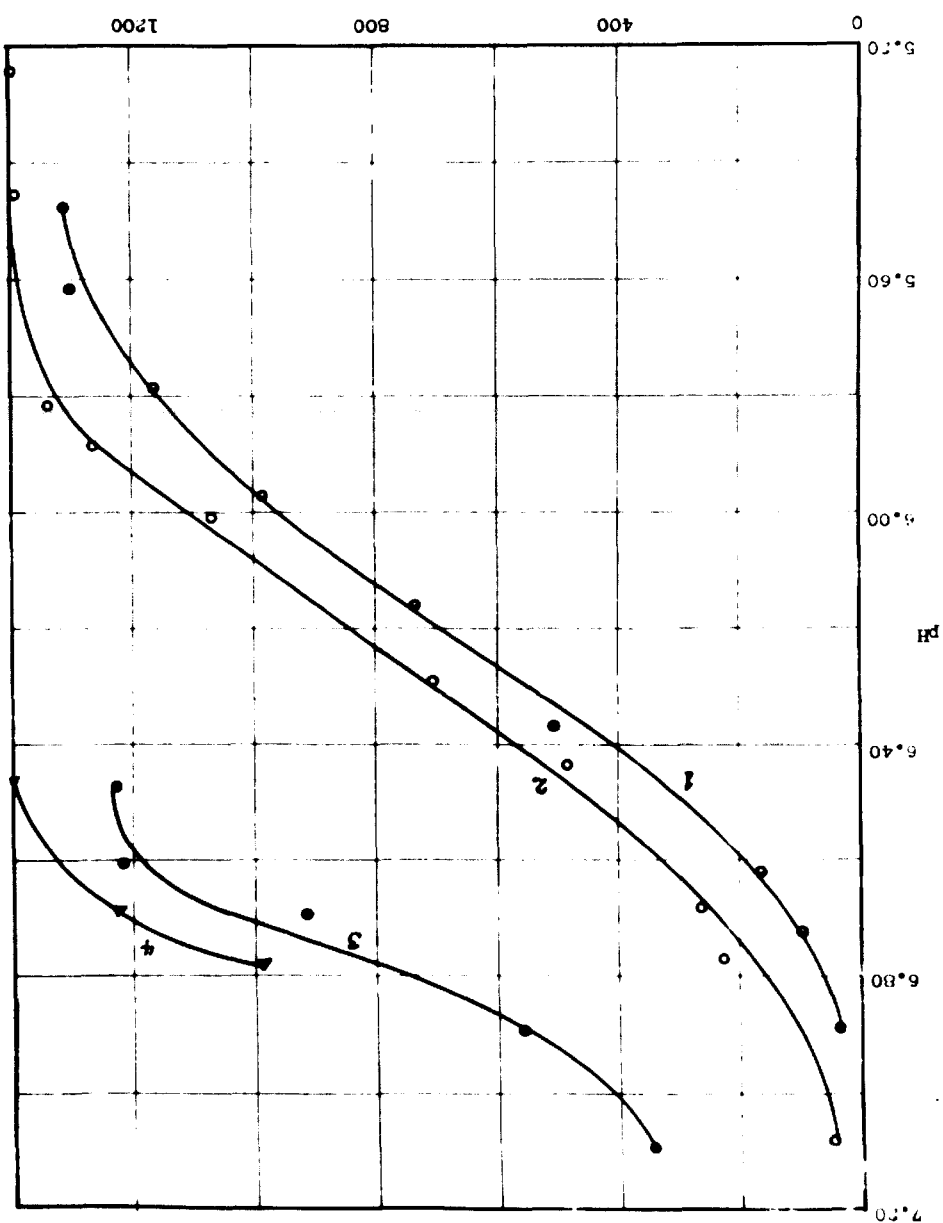


Fig. 2A - Nickel content of buffered nickel sulfate solution at different pH values: 1, NH₄OH treatment, 3 hrs at 100°C.; 2, NH₄OH treatment 24 hrs at 25°C.

Fig. 3 - Cadmium in bottle held solution at different pH values: 1, NaOH treatment, 3 hrs at 100°C.; 2, NH₄OH treatment, 3 hrs at 100°C.; 3, NaOH treatment, 24 hrs at 26°C.; 4, NH₄OH treatment, 24 hrs at 26°C.



Removal of Cadmium from Nickel Sulfate Solution

Table II (a)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l . Cd in soln.
(orig soln)	none	-	485
6.83	24 hrs at 27°C	6.82	485
6.97	"	6.97	470
7.18	"	7.15	490?
7.48	"	7.47	460
6.83	3 hrs at 100°C	6.75	478
6.97	"	6.75	478
7.18	"	6.82	470
7.48	"	7.02	422

Removal of Cadmium from Boric Acid Solution

Table II (c)

pH after addition of NaOH	Treatment	pH after treatment	mg/l. Cd in soln.
(orig soln)	none	-	513
6.95	24 hrs at 24°C	6.93	513
7.09	"	7.12	402
7.24	"	7.27	258
7.40	"	7.44	163
6.05	3 hrs at 100°C	6.13	513
6.26	"	6.24	357
6.41	"	6.34	245
6.58	"	6.52	150
6.75	"	6.70	85
6.95	"	6.93	45
7.09	"	7.13	29
7.24	"	7.32	19
7.40	"	7.47	10

Removal of Cadmium from Boric Acid Solution

Table II (d)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Cd in soln.
(orig soln)	none	-	1400
	24 hrs		
6.44	at 26°C	6.45	1400
6.70	"	6.73	1204
6.79	"	6.79	980
	3 hrs		
5.30	at 100°C	5.38	1400
5.54	"	5.54	1400
5.65	"	5.62	-
5.82	"	5.72	1336
5.93	"	5.76	1256
6.02	"	5.85	1070
6.30	"	6.03	692
6.44	"	6.17	472
6.70	"	6.40	256
6.79	"	6.56	238

Table II (e)

pH after addition of NaOH	Treatment	pH after treatment	mg/l. Cd in soln.
(orig soln)	none	-	1330
	24 hrs		
6.62	at 26°C	6.57	1218
6.74	"	6.73	916
6.90	"	6.91	580
7.09	"	7.13	358
	3 hrs		
5.62	at 100°C	5.63	1334
5.79	"	5.70	1160
5.98	"	5.70	982
6.18	"	5.95	740
6.38	"	6.02	518
6.62	"	6.35	172
6.74	"	6.50	101
6.90	"	6.60	29
7.09	"	6.95	37

Removal of Cadmium from Buffered Nickel Sulfate Solution

Table II (f)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Cd in soln.
(orig soln)	none	-	459
	24 hrs		
6.17	at 2300	6.25	435
6.30	"	6.40	415
6.42	"	6.42	389
6.53	"	6.55	353
6.70	"	6.66	362
6.79	"	6.74	359
6.87	"	6.79	380
	3 hrs		
5.81	at 100°C	5.72	462
5.97	"	5.78	445
6.17	"	5.82	439
6.30	"	5.87	445
6.42	"	5.93	438
6.53	"	6.02	421
6.70	"	6.15	414
6.79	"	6.24	408
6.87	"	6.33	415

Table II (c) cont.

Removal of Cadmium

Solution	After 24 hrs at 52-57°C		After 1 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	none removed	478 mg/l Cd remain pH 6.82	15 mg/l Cd removed pH 7.09	458 mg/l Cd remain pH 7.5
Buffered NiSO ₄	-	380 mg/l Cd remain pH 6.87	-	411 mg/l Cd remain pH 6.87
500 mg/l Cd in H ₃ BO ₃	168 mg/l Cd remain pH 7.40	-	89 mg/l remain pH 7.1 10 mg/l remain pH 7.4	-
1400 mg/l Cd in H ₃ BO ₃	388 mg/l Cd remain pH 7.09	680 mg/l Cd remain pH 6.80	89 mg/l remain pH 6.9 37 mg/l remain pH 7.1	610 mg/l Cd remain pH 6.80

Hexavalent Chromium:- In nickel sulfate solution runs were made with concentrations of 500 and 1000 mg./l. of chromium using ammonium hydroxide to raise the pH. A comparison of curve 1 in Fig. 4 with curve 1 in Fig. 5 shows that the break occurs approximately in the same pH range; namely, 6.5-6.6. Furthermore, a pH of 7.0 is required in both cases to remove chromium almost completely from solution. The previous statement holds true as well in the case of chromium in buffered nickel sulfate as indicated in Fig. 6; however the break in the curve occurs at a lower pH. Noteworthy also is the fact that precipitation from buffered nickel sulfate solution with ammonium hydroxide (upon heating) is more efficient than in unbuffered nickel sulfate solution until a pH of 6.8 is reached, whereupon the two curves tend to approach one another. The voluminous precipitation of nickel hydroxide in the buffered solution probably carries down some chromium with it. It seems doubtful that the boric acid has any influence in this case, since, as Table III (d) shows, hexavalent chromium does not precipitate at all from a boric acid solution up to a pH of 7.1 using ammonium hydroxide.

With sodium hydroxide as precipitant a small quantity of light yellow needles was noted at pH 7.0 after the solution had been heated 5 hours at 100°C. The solution changed progressively from an orange-red at pH 5 to a light yellow as sodium hydroxide was added, indicating

the conversion of the chromic acid to sodium chromate.

Trivalent Chromium:- Initial appearance of turbidity upon adding ammonium or sodium hydroxide to a nickel sulfate solution containing the chromic sulfate was observed very near pH 4.6. This value was quite reproducible if the additions of base were made slowly and the solution well agitated. Upon heating a series at different pH values, increase in acidity of the solution was noted as shown in Tables IV (a), (b), (c), etc. The interesting fact is that where the initial pH values for nickel sulfate solution lie in the approximate range of 3.4-4.9 the values after heating for 3 hours at 100°C all drop to pH 2.6 ± 0.1 . When the pH's of the heated samples begin to rise above 2.7, the concentration of chromium decreases rapidly. Thus, only an approximation of the pH value at which the chromium is removed is gained from these measurements.

In the case of the samples heated at 100°C there was considerable difficulty in obtaining consistent data concerning the minimum point at which precipitation occurs after 3 hours. After five trials using ammonium hydroxide as precipitant the best information available is that the range is probably below pH 2.0. The inconsistent results are thought to be associated with rate of hydrolysis of the chromic sulfate.

Britton and Wescott (12) carried out titrations of 0.5N chromic salts with 2.0N NaOH. They observed an

increase in acidity upon heating the salt solution as shown by the fact that a 0.5M $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ solution had a pH of 2.85, but when heated to boiling and cooled, the pH had dropped to pH 1.2.

Inspection of Table IV (g) shows that in boric acid solution chromium hydroxide starts to precipitate at a lower pH than in the buffered and unbuffered nickel sulfate.

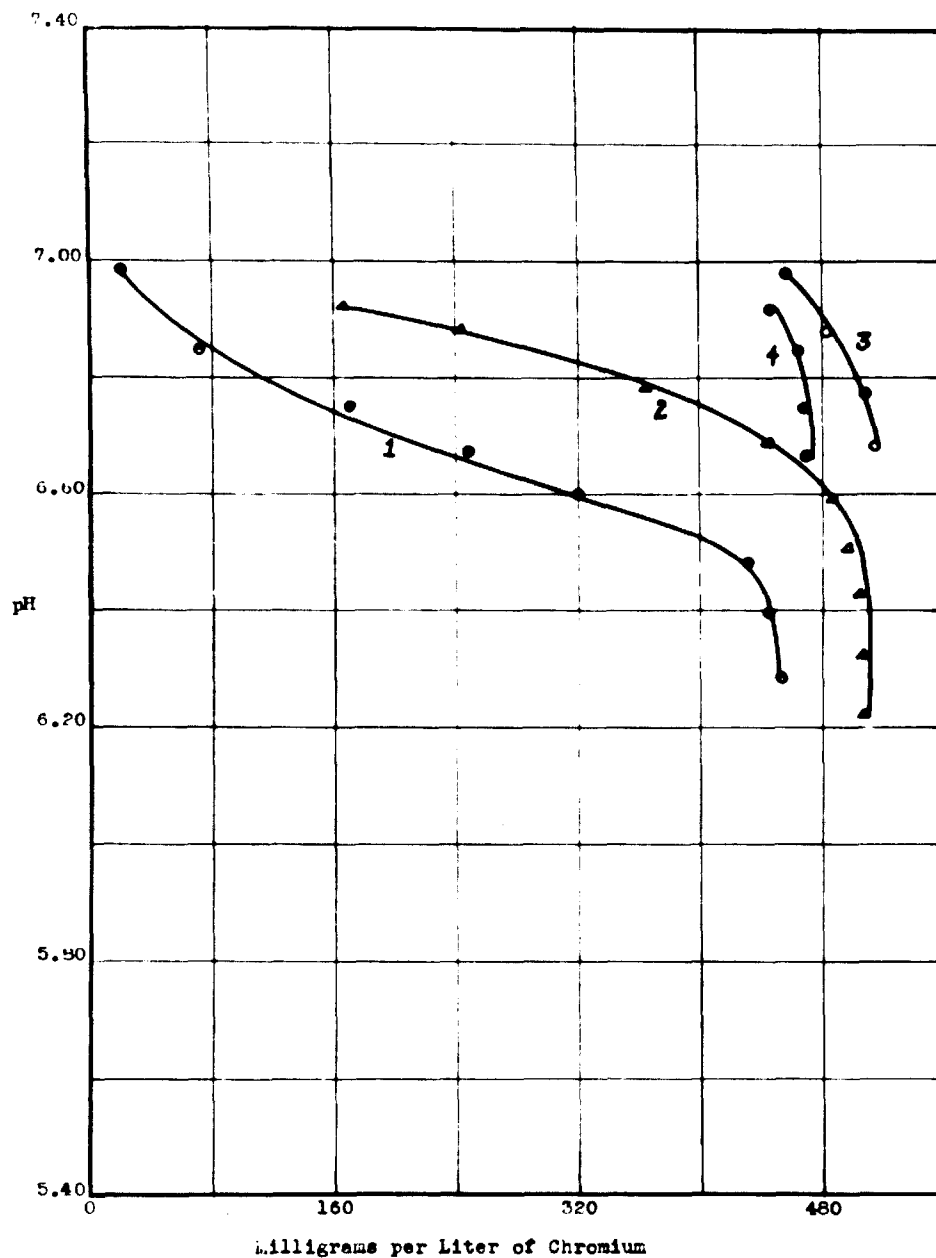


Fig. 4 - Hexavalent chromium in nickel sulfate solution at different pH values: 1, NH_4OH treatment, 3 hrs at 100°C .; 2, NaOH treatment, 3 hrs at 100°C .; 3, NH_4OH treatment, 24 hrs at 23°C .; 4, NaOH treatment, 24 hrs at 22°C .

Removal of Hexavalent Chromium from Nickel Sulfate Solution

Table III (c)

PH after addition of NH_4OH Treatment PH after treatment in solution MS/L. 10^{-6}

477	-	none	24 hrs	6.33	477
477	6.33	"	at 2700	6.39	477
477	6.37	"	"	6.48	477
477	6.50	"	"	6.50	477
477	6.57	"	"	6.57	477
477	6.73	"	"	6.73	477
477	6.81	"	"	6.81	477
477	6.97	"	"	6.97	477
458	6.33	at 10000	24 hrs	6.33	458
458	6.38	"	"	6.38	458
458	6.47	"	"	6.47	458
458	6.48	"	"	6.48	458
458	6.52	"	"	6.52	458
458	6.60	"	"	6.60	458
458	6.65	"	"	6.65	458
458	6.76	"	"	6.76	458

(only soln)

Removal of Hexavalent Chromium from Nickel Sulfate Solution

Table III (b)

pH after addition of NaOH	Treatment	pH after treatment	mg/l. Cr ⁶ in soln.
(orig soln)	none	--	522
	24 hrs at 200C		
6.22	"	6.17	522
6.32	"	6.23	522
6.42	"	6.00?	522
6.50	"	6.37	512
6.59	"	6.46	522
6.69	"	6.55	520
6.78	"	6.62	515
6.88	"	6.69	487
6.92	"	6.68	480
	3 hrs at 100C		
6.22	"	5.92	517
6.32	"	5.98	511
6.42	"	6.10	509
6.50	"	6.07	506
6.59	"	6.38	492
6.69	"	6.44	449
6.78	"	6.17	367
6.88	"	6.58	247
6.92	"	6.65	169

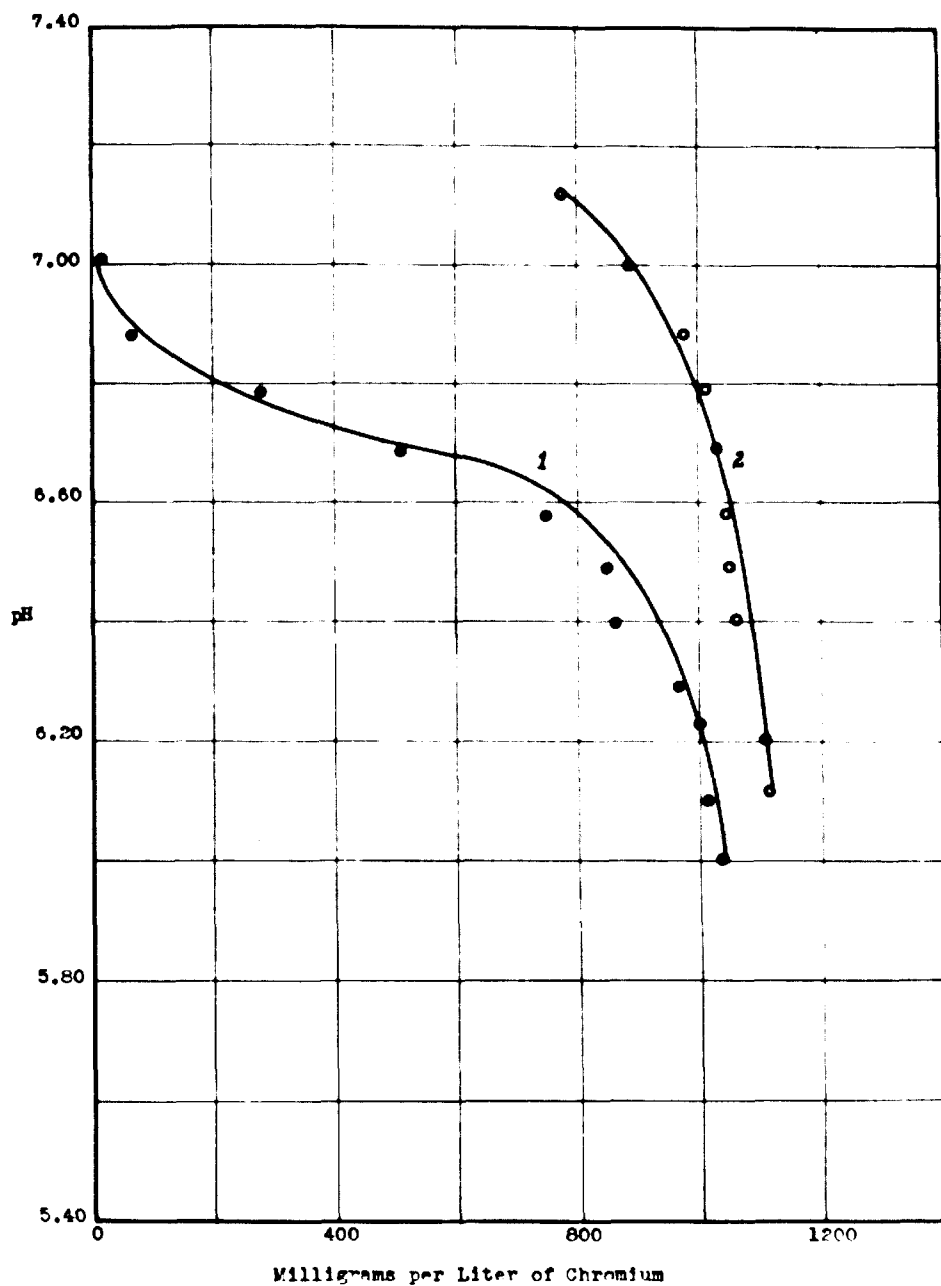


Fig. 5 - Hexavalent chromium in nickel sulfate solution at different pH values: 1, NH_4OH treatment, 3 hrs at 100°C .; 2, NH_4OH treatment, 24 hrs at 24°C .

Removal of Hexavalent Chromium
from Nickel Sulfate Solution

Table III (c)

pH after addition of H_2O_2	Treatment	pH after treatment	mg/l. Cr^{6+} in soln.
(orig soln)	none	-	1,110
	24 hrs at 24°C		
6.40	"	6.45	1,059
6.49	"	6.49	1,044
6.56	"	6.55	1,046
6.69	"	6.68	1,030
6.79	"	6.73	1,015
6.88	"	6.82	982
7.01	"	6.94	934
7.13	"	7.02	771
	3 hrs at 100°C		
6.00	"	6.05	1,040
6.10	"	-	1,010
6.15	"	6.22	1,003
6.29	"	-	967
6.40	"	5.98	866
6.49	"	6.08	852
6.58	"	6.16	737
6.69	"	6.29	515
6.79	"	6.44	382
6.88	"	6.68	68
7.01	"	-	16
7.13	"	6.72	spoiled

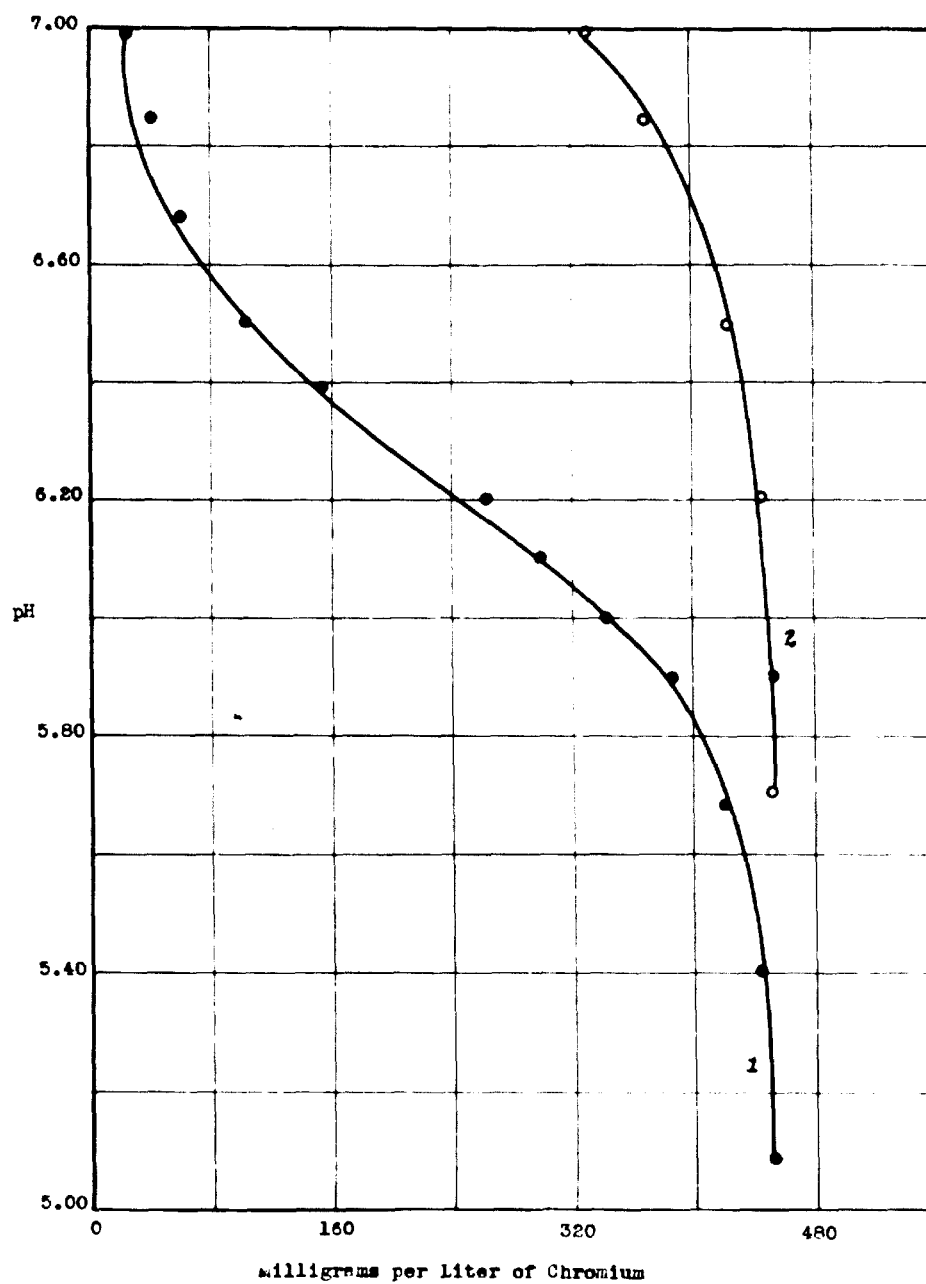


Fig. 6 - Hexavalent chromium in buffered nickel sulfate solution at different pH values: 1, NH_4OH treatment, 3 hrs at 100°C .; 2, NH_4OH treatment, 24 hrs at 24°C .

Removal of Hexavalent Chromium from
Buffered Nickel Sulfate Solution

Table III (a)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Cr ⁶⁺ in soln.
(orig soln.)	none	-	454
5.90	24 hrs at 24°C	5.87	434
6.00	"	6.07	-
6.10	"	6.16	-
6.20	"	6.10	449
6.39	"	6.38	-
6.50	"	6.47	423
6.68	"	6.57	-
6.85	"	6.85	372
7.00	"	7.02	332
5.08	24 hrs at 100°C	5.11	455
5.40	"	5.39	448
6.68	"	5.52	424
5.90	"	5.67	390
6.00	"	5.80	346
6.10	"	5.84	302
6.20	"	5.88	266
6.39	"	5.96	154
6.50	"	6.02	105
6.68	"	6.23	61
6.85	"	6.37	42
7.00	"	6.41	25

Summary of Data on Hexavalent Chromium

Table III (f)

Appearance of Turbidity

Solution	After addition of base		After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH	NaOH	NH ₄ OH
500 mg/l Cr in NiSO ₄	?	clear pH 7.0	6.6 - 6.7	6.8 - 6.9	6.2 - 6.3	6.1 - 6.2
1000 mg/l Cr in NiSO ₄	-	6.9 - 7.0	-	6.2 - 6.5	-	below pH 6.0
H ₂ BO ₃	clear pH 7.1	clear pH 7.1	clear pH 7.1	clear pH 7.1	clear pH 7.1	clear pH 7.1
Buffered NiSO ₄	-		-		-	

Heavy Precipitation

Solution	After addition of base		After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH	NaOH	NH ₄ OH
500 mg/l Cr in NiSO ₄	above pH 7.0	clear pH 7.0	above pH 6.9	none pH 7.0	above pH 6.6	above pH 6.6
1000 mg/l Cr in NiSO ₄	-	none pH 7.1	-	above pH 6.7	-	above pH 6.7
H ₂ BO ₃	none pH 7.1	none pH 7.1	none pH 7.1	none pH 7.1	none pH 7.1	none pH 7.1
Buffered NiSO ₄	-		-		-	

Table III (f) cont.

Removal of Chromium

Solution	After 24 hrs at 25-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH
500 mg/l Cr in NiSO ₄	50 mg/l Cr removed pH 6.9	17 mg/l Cr removed pH 6.98	170 mg/l Cr remain pH 6.9	28 mg/l Cr remain pH 6.96
1000 mg/l Cr in NiSO ₄	-	770 mg/l remain pH 7.1	-	16 mg/l Cr remain pH 7.0
H ₃ PO ₃	none removed pH 7.1	none removed pH 7.1	none removed pH 7.1	none removed pH 7.1
Buffered NiSO ₄	-	120 mg/l removed pH 7.0	-	42 mg/l re- main pH 6.85 24 mg/l re- main pH 7.0

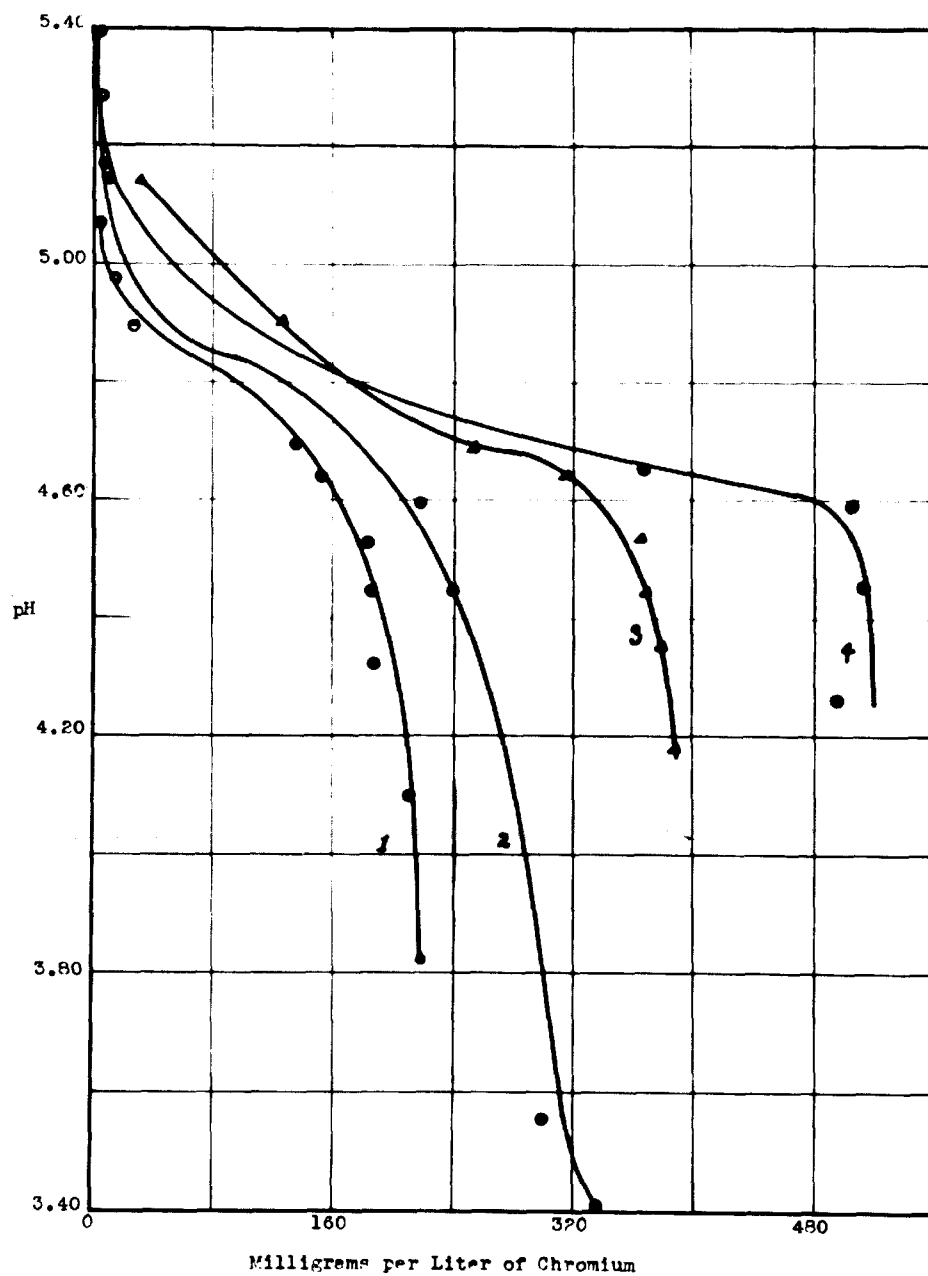


Fig. 7 - Trivalent chromium in nickel sulfate solution at different pH values: 1, NaOH treatment, 3 hrs at 100°C; 2, NH₄OH treatment, 3 hrs at 100°C.; 3, NaOH treatment, 24 hrs at 25°C; 4, NH₄OH treatment, 24 hrs at 24°C.

Removal of Trivalent Chromium
from Nickel Sulfate Solution

Table IV (a)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Cr^{3+} in soln
(orig soln)	none	-	505
	24 hrs at 100°C		
4.56	"	3.88	487
4.55	"	3.89	504
4.59	"	3.92	505
4.65	"	4.08	368
4.68	"	4.10	256
4.92	"	4.51	spoiled
5.17	"	4.89	5
5.27	"	5.00	4
5.30	"	5.21	3
	3 hrs at 100°C		
3.10	"	2.64	379
3.52	"	2.65	304
4.05	"	2.65	spoiled
4.26	"	2.65	"
4.45	"	2.65	240
4.59	"	2.65	218
4.92	"	3.13	9
5.17	"	3.46	4
5.27	"	3.82	3

Table IV (b)

pH after addition of NaOH	Treatment	pH after treatment	mg/l. Cr^{3+} in soln
(orig soln)	none	-	367
	24 hrs at 100°C		
4.18	"	3.78	382
4.42	"	3.81	377
4.42	"	3.87	372
4.52	"	3.94	372
4.63	"	4.00	316
4.68	"	4.09	256
4.90	"	4.25	130
5.15	"	4.37	34
	3 hrs at 100°C		
3.82	"	2.65	224
4.02	"	2.64	218
4.53	"	2.63	184
4.42	"	2.64	189
4.52	"	2.67	183
4.63	"	2.67	156
4.68	"	2.68	136
4.90	"	2.74	29
5.15	"	2.95	1

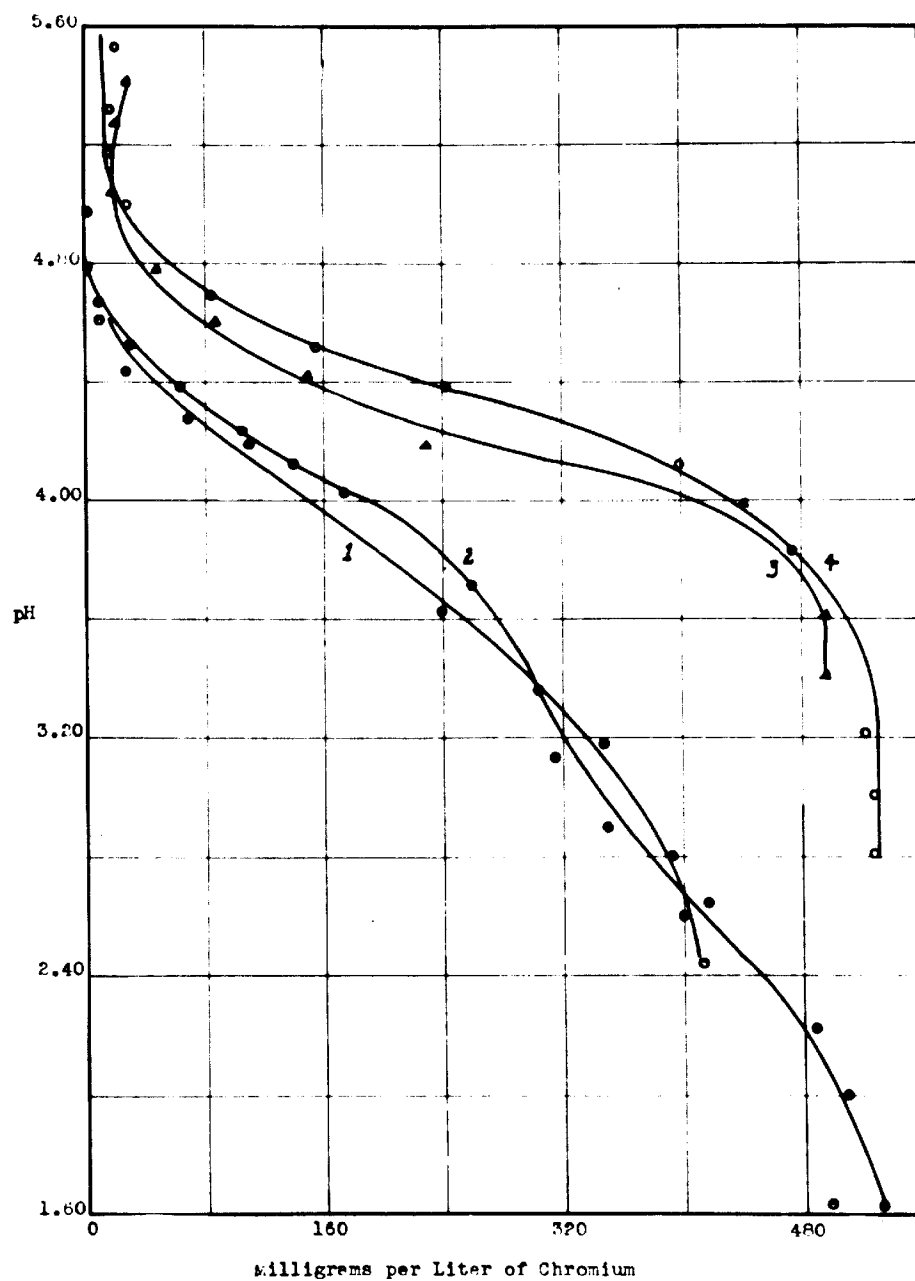


Fig. 8 - Trivalent chromium in boric acid solution at different pH values: 1, NH_4OH treatment, 3 hrs at 100°C .; 2, NaOH treatment, 3 hrs. at 100°C .; 3, NH_4OH treatment, 24 hrs at 24°C .; 4, NaOH treatment, 24 hrs at 24°C .

Removal of Trivalent Chromium
from Boric Acid Solution

Table IV (d)

pH after addition of NaOH	Treatment	pH after treatment	mg/l. Cr ³⁺ in soln.
(orig soln)	none	-	534
	24 hrs at 24°C		
3.21	"	3.30	525
3.70	"	3.42	482
3.83	"	3.49	479
4.05	"	3.55	spoiled
4.12	"	3.60	402
4.32	"	3.72	244
4.51	"	3.81	157
4.67	"	4.02	75
4.98	"	4.40	19
5.13	"	4.77	15
5.22	"	5.10	17
5.33	"	5.40	21
	5 hrs at 100°C		
1.93	"	2.12	512
2.20	"	2.32	421
2.63	"	2.48	420
2.92	"	2.49	spoiled
3.12	"	2.52	316
3.35	"	2.52	304
3.70	"	2.53	267
3.83	"	2.59	164
4.02	"	2.61	174
4.12	"	2.64	141
4.23	"	2.64	105
4.38	"	2.73	64
4.52	"	2.81	28
4.67	"	3.23	7
4.98	"	3.99	0
5.13	"	4.38	0

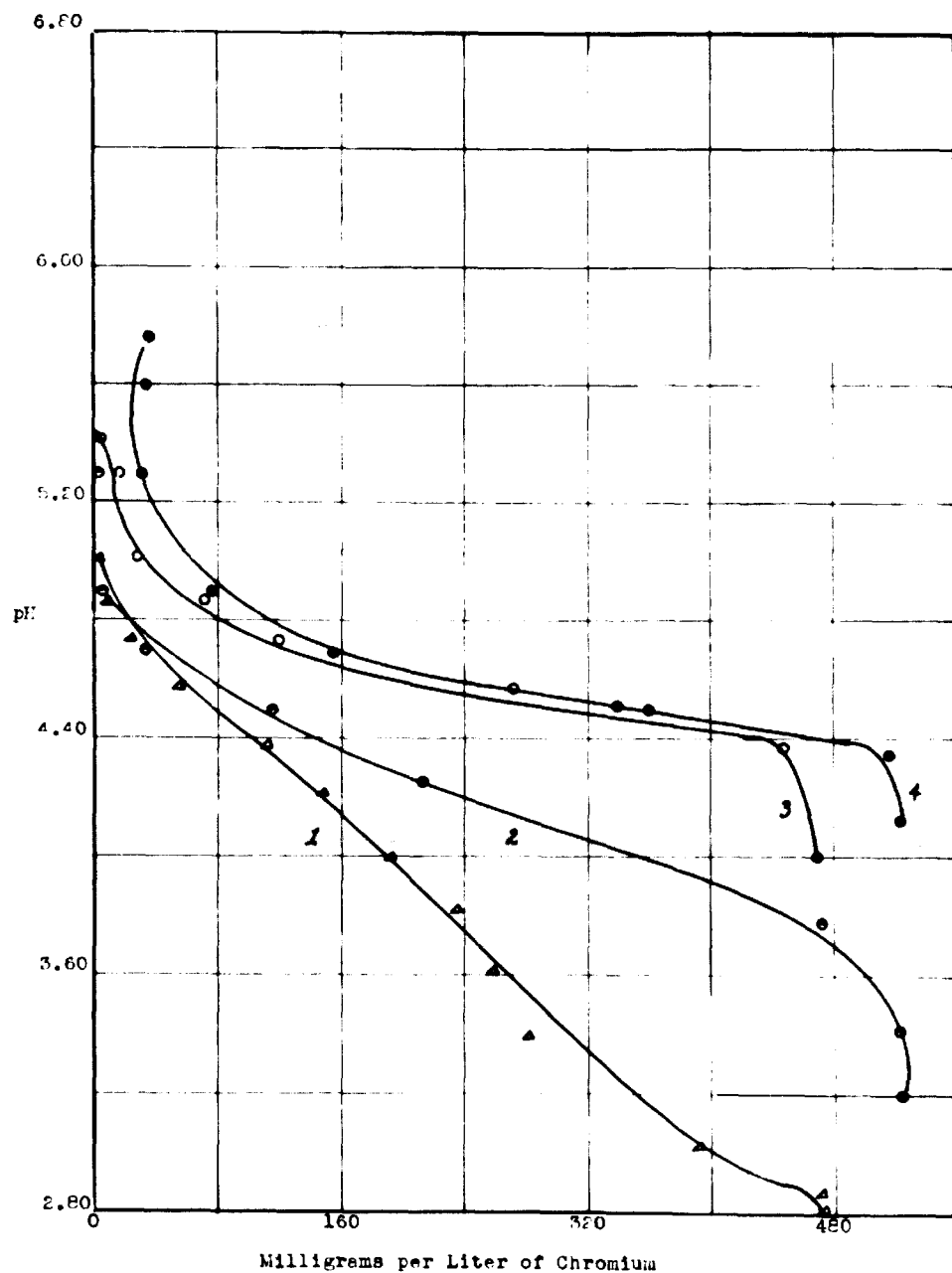


Fig. 2 - Trivalent chromium in buffered nickel sulfate solution at different pH values: 1, NaOH treatment, 3 hrs at 100°C.; 2, NH₄OH treatment, 3 hrs at 100°C.; 3, NaOH treatment, 24 hrs at 25°C.; 4, NH₄OH treatment, 24 hrs at 25°C.

Removal of Trivalent Chromium from
Buffered Nickel Sulfate Solution

Table IV (e)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Cr^{3+} in soln.
(orig soln)	none	-	523
	24 hrs		
4.35	at 23°C	4.00	515
4.50	"	4.16	361
4.70	"	4.46	156
4.90	"	4.79	77
5.30	"	5.23	35
5.60	"	5.62	34
5.75	"	5.78	37
	3 hrs		
	at 100°C		
5.42	"	2.62	524
5.78	"	2.65	471
5.95	"	2.62	spoiled
4.25	"	2.64	214
4.50	"	2.68	113
4.70	"	2.95	34
4.90	"	3.62	5
5.30	"	4.90	2
5.60	"	5.50	0

Removal of Trivalent Chromium from
Buffered Nickel Sulfate Solution

Table IV (f)

pH after addition of NaOH	Treatment	pH after treatment	mg/l. Cr^3 in soln.
(orig soln)	none	-	468
	24 hrs at 23°C		
4.38	"	4.02	449
4.51	"	4.17	340
4.58	"	4.27	255
4.74	"	4.42	120
4.87	"	4.67	71
5.02	"	4.97	28
5.30	"	5.28	16
5.42	"	5.45	4
	3 hrs at 100°C		
2.89	"	2.55	472
3.13	"	2.58	393
3.40	"	2.58	284
3.62	"	2.61	259
3.82	"	2.61	234
4.00	"	2.59	194
4.25	"	2.59	150
4.38	"	2.61	112
4.58	"	2.69	55
4.74	"	2.91	19
4.87	"	3.17	9
5.02	"	3.72	2
5.30	"	4.88	0
5.42	"	4.65	0

Summary of Data on Trivalent Chromium

Table IV (g)

Appearance of Turbidity

Solution	After addition of base		After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	4.5-4.6	4.5-4.7	4.4-4.5	4.4-4.5	3.1-3.4	below pH 3.0
H ₃ BO ₃	3.7-3.8	3.8-3.9	3.6-3.7	3.3-3.6	1.8-2.0	below pH 2.0
Buffered NiSO ₄	4.6-4.7	4.8-4.9	4.4-4.5	4.35-4.50	2.8-2.9	3.4-3.7

Heavy Precipitation

Solution	After addition of base		After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	4.6-4.7	4.6-4.7	4.5-4.6	above 4.5-4.6	above pH 3.8	above 3.8-2.9
H ₃ BO ₃	above pH 4.1	above pH 4.0	above 3.9-4.0	above 3.8-3.9	above 2.8-2.9	above pH 2.8
Buffered NiSO ₄	above 4.7-4.9	above 5.0-5.1	above pH 4.6	above 4.6-4.7	above 3.6-3.7	above 3.8-3.9

Removal of Chromium

Solution	After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	34 mg/l Cr remain pH 5.15	5 mg/l Cr remain pH 5.2	removed pH 5.1 - 5.2	9 mg/l remain pH 5.0 3 mg/l remain pH 5.3
H ₃ BO ₃	20 mg/l remain pH 5.0 and 5.5	16 mg/l remain pH 5.1 28 mg/l remain pH 5.4	7 mg/l remain pH 4.7 Cr removed 4.7-4.9	7 mg/l remain pH 4.6 Cr removed 4.7-4.8
Buffered NiSO ₄	16 mg/l remain pH 5.3 4 mg/l remain pH 5.4	20 mg/l remain pH 5.3 37 mg/l remain pH 5.75	9 mg/l remain pH 4.9 Cr removed 5.0-5.2	34 mg/l remain pH 4.7 5 mg/l remain pH 4.9

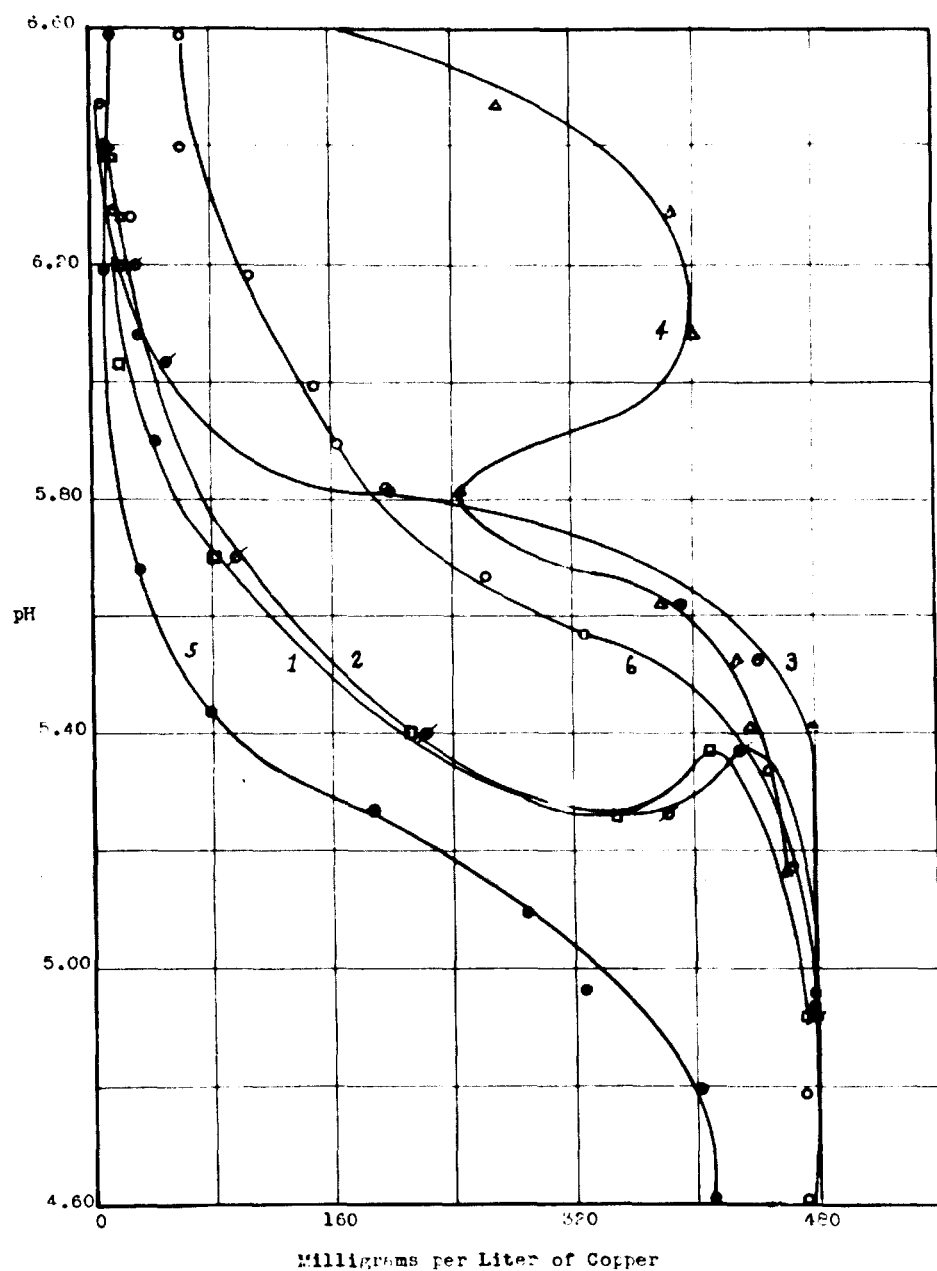


Fig. 10 - Copper in buffered and unbuffered nickel sulfate solutions at different pH values: 1, nickel sulfate solution after NaOH treatment, 3 hrs at 100°C.; 2, nickel sulfate solution after NaOH treatment, 24 hrs at 27°C.; 3, nickel sulfate solution after NH_4OH treatment, 4 hrs at 100°C.; 4, nickel sulfate solution after NH_4OH treatment, 24 hrs at 25°C.; 5, buffered nickel sulfate solution after NH_4OH treatment, 3 hrs at 100°C.; 6, buffered nickel sulfate solution after NH_4OH treatment, 24 hrs at 24°C.

Removal of Copper from Nickel Sulfate Solution

Table V (a)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Cu in soln.
(orig soln)	none	-	480
	74 hrs		
5.17	at 24°C	5.15	465
5.41	"	5.00	438
5.52	"	5.05	435
5.62	"	5.07	378
5.81	"	5.30	248
6.08	"	6.07	101
6.29	"	6.30	390
6.47	"	6.50	230
6.69	"	6.69	212
6.82	"	6.84	136
6.98	"	7.02	30
	6 hrs		
4.65	at 100°C	4.60	443
4.94	"	4.68	478
5.17	"	4.85	467
5.41	"	4.92	478
5.52	"	4.92	445
5.62	"	4.53	394
5.81	"	5.12	198
6.08	"	5.20	35
6.29	"	6.15	14
6.47	"	6.39	8
6.69	"	6.66	2
6.82	"	6.69	3
6.98	"	6.73	2
6.98	"	6.75	2

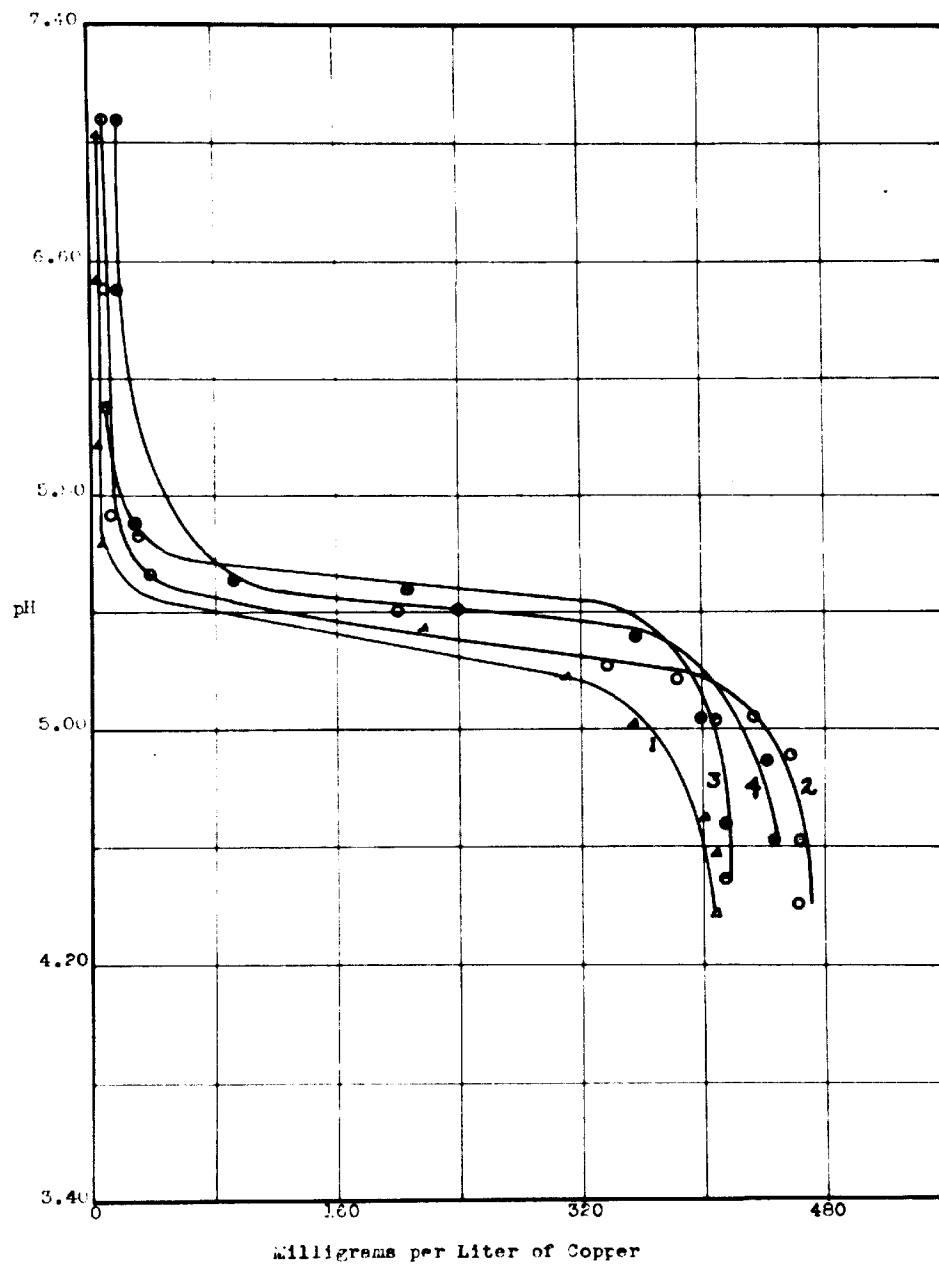


FIG. 11- Copper in boric acid solution at different pH values: 1, NaOH treatment, 3 hrs at 100°C.; 2, NH₄OH treatment, 3 hrs at 100°C.; 3, NaOH treatment, 24 hrs at 25°C.; 4, NH₄OH treatment, 24 hrs at 25°C.

Removal of Copper from Boric Acid Solution

Table V (c)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Cu in soln.
(orig soln)	none	-	470
	24 hrs at 25°C		
4.62	"	4.82	467
4.85	"	4.81	467
5.04	"	5.02	462
5.14	"	4.98	398
5.32	"	5.00	362
5.38	"	4.99	-
5.40	"	5.02	339
5.40	"	5.05	97
5.68	"	5.71	17
6.50	"	6.55	7
6.75	"	6.61	9
7.02	"	7.06	-
7.12	"	7.21	10
	3 hrs at 100°C		
4.46	"	4.62	460
4.62	"	5.92	475
4.85	"	5.85	468
5.04	"	5.97	435
5.14	"	4.86	-
5.18	"	4.00	335
5.32	"	4.10	318
5.38	"	4.10	-
5.40	"	4.72	196
5.50	"	4.85	40
5.68	"	5.60	6
6.10	"	6.50	3
6.75	"	6.78	6
7.12	"	7.12	7

Removal of Copper from Peric Acid Solution

Table V (d)

pH after addition of NaOH	Treatment	pH after treatment	mg/l. Cu in soln.
(orig soln)	none	-	407
	24 hrs at 25°C		
4.74	"	4.70	420
5.02	"	5.00	-
5.12	"	4.98	410
5.22	"	4.98	384
5.33	"	4.99	340
5.47	"	5.08	216
5.63	"	5.31	85
5.95	"	5.98	7
	3 hrs at 100°C		
4.55	"	4.12	417
4.74	"	4.19	400
4.85	"	4.20	-
5.02	"	4.21	350
5.22	"	4.21	318
5.33	"	4.28	264
5.63	"	5.52	5
5.95	"	5.95	4
6.25	"	6.40	-
6.50	"	6.68	-
6.69	"	7.05	-
7.12	"	7.28	2

Removal of Copper from
Buffered Nickel Sulfate Solution

Table V (e)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Cu in soln.
(orig soln)	none	-	485
	24 hrs at 24°C		
4.30	"	4.62	491
4.97	"	4.83	494
5.10	"	5.02	484
5.27	"	5.20	482
5.35	"	5.28	458
5.48	"	5.35	334
5.66	"	5.57	268
5.83	"	5.70	201
5.90	"	5.75	166
6.00	"	5.82	151
6.19	"	6.00	106
6.41	"	6.23	61
6.62	"	6.45	34
	24 hrs at 100°C		
4.30	"	4.10	463
4.62	"	4.12	424
4.80	"	4.32	415
4.97	"	4.35	341
5.10	"	4.48	301
5.27	"	4.55	197
5.44	"	4.72	85
5.68	"	5.18	37
5.90	"	5.56	44
6.00	"	5.68	27
6.19	"	5.82	9
6.41	"	5.97	8
6.62	"	6.07	11

Summary of Data on Copper

Table V (f)

Appearance of Turbidity

Solution	After addition of base		After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	5.0-5.10	5.1-5.3	4.8-4.9	4.9-5.1	below pH 4.9	4.4-4.6
HgBO ₃	5.2-5.3	5.3-5.4	5.0-5.1	5.0-5.1	4.6-4.7	4.6-4.8
Buffered NiSO ₄	-	5.6-5.7	-	5.0-5.1	-	below pH 4.6

Heavy Precipitation

Solution	After addition of base		After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	above pH 5.3	above pH 5.6	above pH 5.2	above pH 5.5	above pH 5.3	above pH 5.6
HgBO ₃	above pH 5.4	above pH 5.4	above pH 5.2	above pH 5.2	above pH 4.9	above pH 4.9
Buffered NiSO ₄	-	above pH 5.7	-	above pH 4.7	-	above pH 5.4

Removal of Copper

Solution	After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	21 mg/l remain pH 6.0 15 mg/l remain pH 6.4	30 mg/l remain pH 7.0	30 mg/l remain pH 6.2 11 mg/l remain pH 6.4	35 mg/l remain pH 6.1 9 mg/l remain pH 6.5
HgBO ₃	28 mg/l remain pH 6.3 7 mg/l remain pH 6.0	17 mg/l remain pH 6.7 10 mg/l remain pH 7.1	5 mg/l remain pH 6.3	40 mg/l remain pH 6.5 6 mg/l remain pH 6.7
Buffered NiSO ₄	-	24 mg/l remain pH 6.6	-	27 mg/l remain pH 6.0 11 mg/l remain pH 6.6

Ferrous Iron:- Keeping ferrous iron in the reduced state under the conditions adopted for these runs was a matter of some difficulty. A number of trials were made before it was possible to obtain fairly consistent results.

The solution was placed in a one liter three neck flask and a rapid stream of hydrogen from a Kipp generator passed through it while the samples were being collected. Two purification trains consisting of alkaline pyrogalllic acid, potassium permanganate and distilled water were placed in series with the Kipp generator. As soon as the samples were withdrawn from the flask they were placed in test tubes connected in series to a tank of nitrogen. A rapid stream of gas was bubbled through the solution for two minutes, then the rate was reduced to about 2 - 3 bubbles per second for the duration of the treatment. Even with these precautions some oxidation to ferric iron occurred. Curves 1 and 2 in Fig. 12, however, show definitely that ferrous iron is not removed at pH 6.8 although precipitation started between pH 5.0 and 5.4.

Because of the difficulties involved, and because of the fact that ferrous iron is readily oxidized completely to the ferric state and removed from solution in this form, further experiments with ferrous iron were abandoned.

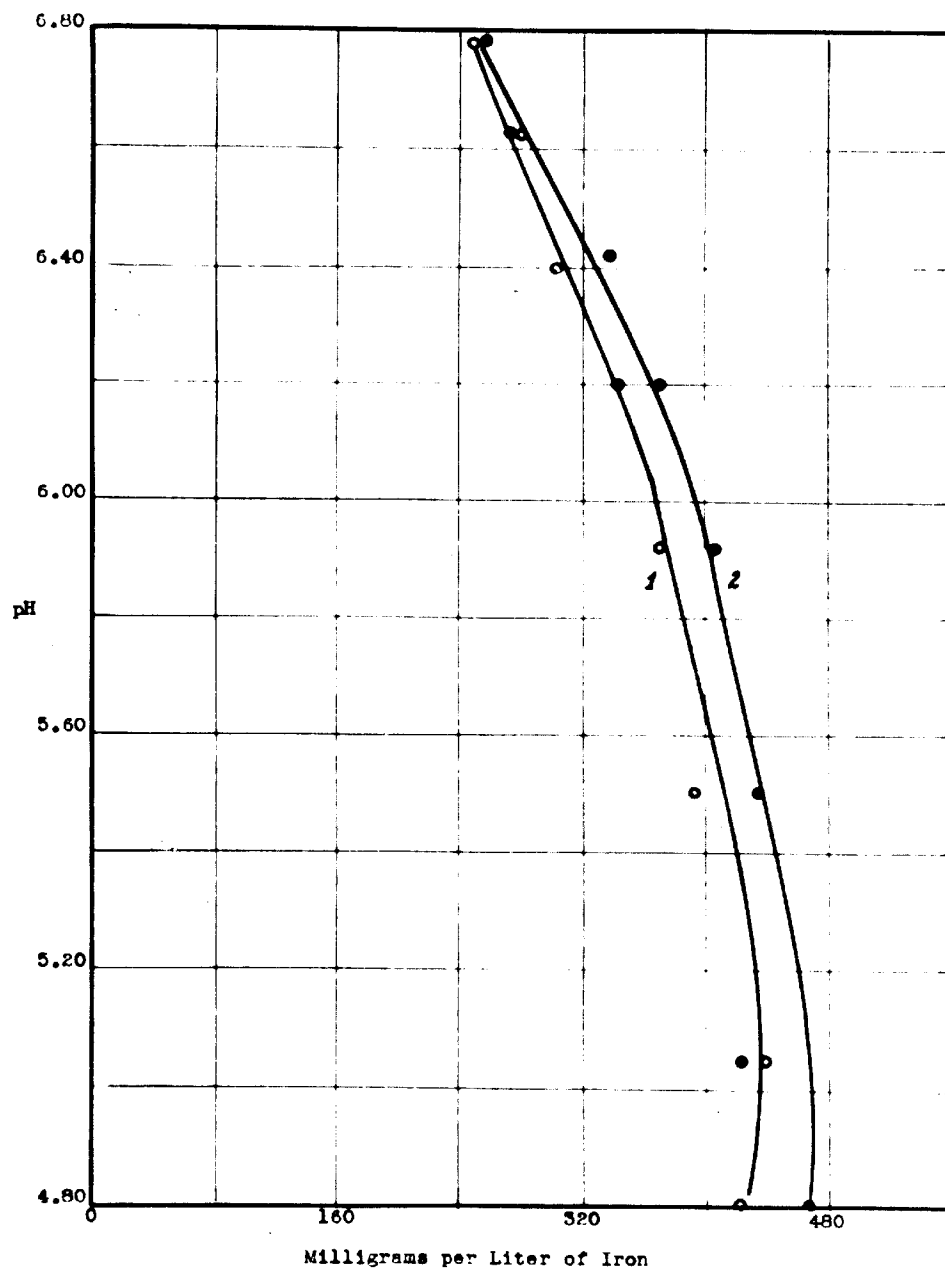


Fig. 12 - Ferrous iron in nickel sulfate solution at different pH values: 1, NH_4OH treatment, 24 hrs at 26°C .; 2, NH_4OH treatment, 3 hrs at 100°C .

Removal of Ferrous Iron from Nickel Sulfate Solution

Table VI (a)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Fe^{2+} in soln.
(orig soln)	none	-	485
	24 hrs at 26°C		
4.48	"	4.45	526
4.78	"	4.67	422
5.05	"	4.93	440
5.50	"	5.32	395
5.95	"	5.78	372
6.20	"	6.10	346
6.42	"	6.33	302
6.65	"	6.52	279
6.78	"	6.75	250
	3 hrs at 100°C		
4.52	"	4.50	468
4.78	"	4.90	470
5.05	"	5.00	423
5.50	"	5.39	456
5.92	"	5.80	410
6.20	"	6.02	372
6.42	"	6.25	348
6.65	"	6.40	275
6.78	"	6.55	258

Ferric Iron:- A boric acid solution containing 500 mg/l ferric iron at pH 1.4-1.5 was colorless. As the pH was raised with ammonium or sodium hydroxide a light yellow coloration appeared at about pH 1.9, which rapidly changed to dark orange as further additions of base were made. No visible turbidity was observed however, until a pH of 2.6-2.7 was reached, although the solutions between pH 1.9 and 2.6 showed the Tyndall effect. Further additions of alkali brought about precipitation of hydrous ferric oxide without raising the pH appreciably until most of the iron was removed. Small quantities of base then caused large increases in the pH of the solution.

Upon heating a series at 100°C coagulation and voluminous precipitation was observed in all samples above pH 1.9 after five minutes in the water bath. Over the period of 5 hours the samples below this pH showed precipitation down to pH 1.6-1.7. Between pH 1.5 and 1.6 the solutions were turbid, but no settled precipitate was present. At pH 1.4 the sample was clear.

The appearance of the colloidal stage in the buffered and unbuffered nickel sulfate solutions was at a much higher value than in the case of boric acid alone. The solutions became yellow green between pH 2.8 and 3.0. Above this range rather large additions of alkali served largely to bring more ferric sulfate into the colloidal state without effecting the pH to any appreciable extent. When pH 3.1-3.3 was reached, heavy turbidity was noted

and furthermore, small additions of alkali caused a marked decrease in the acidity.

Curves 3 and 4 of Fig. 15 are interesting in that there is actually a narrow pH range between 3.0 and 3.1 in which the colloidal hydrous ferric oxide is stable for 36 to 48 hours. On either side of this range precipitation occurred in less than 24 hours. Colloidal hydrous ferric oxide in nickel sulfate solution did not show this degree of stability.

In Figs. 13, 14, and 15 it may be noted that approximately 80% of the iron is removed in the heated samples as low as pH 2.0 - 2.1; however, in order to effect complete or nearly complete removal, the pH must be raised well above this range.

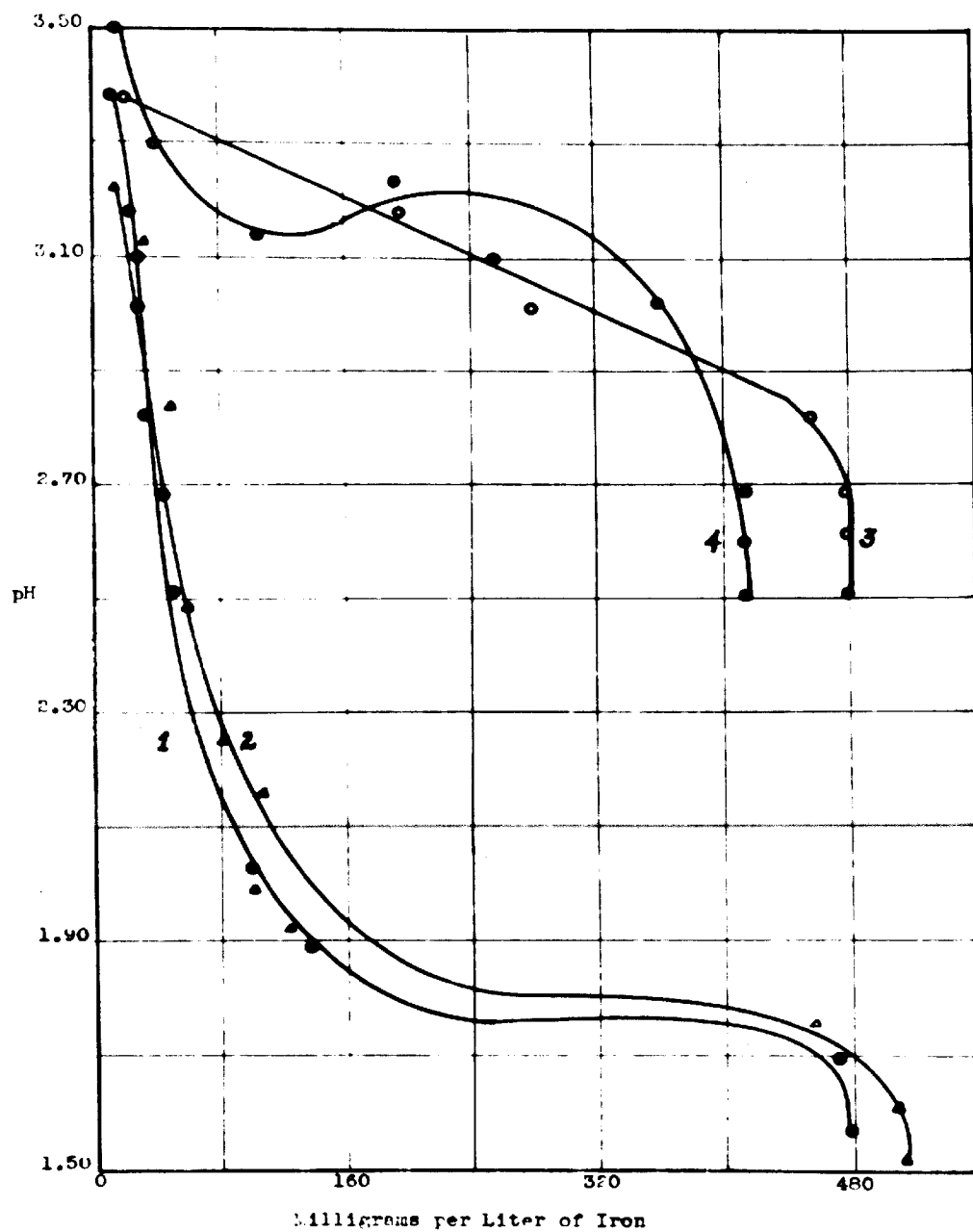


Fig. 13 - Ferric iron in nickel sulfate solution at different pH values:
 1, NaOH treatment, 3 hrs at 100°C.; 2, NH₄OH treatment, 3 hrs at 100°C.;
 3, NaOH treatment, 24 hrs at 24°C.; 4, NH₄OH treatment, 24 hrs at 26°C.

Removal of Ferric Iron from Nickel Sulfate Solution

Table VII (a)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Fe^{3+} in soln.
(orig soln)	none	-	420
2.68	24 hrs at 260°C	2.65	417
3.02	"	2.78	363
3.25	"	2.76	195
3.15	"	2.88	103
3.30	"	3.09	32
3.42	"	3.31	23
3.52	"	3.41	8
(orig soln)	none	-	520
1.49	3 hrs at 100°C	1.47	520
1.59	"	1.55	510
1.75	"	1.65	460
1.91	"	1.73	124
1.98	"	1.74	100
2.15	"	1.88	103
2.34	"	1.94	80
2.48	"	2.02	58
2.55	"	2.14	47
3.12	"	2.78	28
3.25	"	2.75	10
3.49	"	3.13	7
3.65	"	3.05	0

Removal of Ferric Iron from Nickel Sulfate Solution

Table VII (b)

pH after addition of NaOH	Treatment	pH after treatment	mg/l. Fe^3 in soln
(orig soln)	none	-	480
	24 hrs at 27°C		
2.51	"	2.42	430
2.61	"	2.53	430
2.68	"	2.62	480
2.82	"	2.78	458
2.90	"	2.85	400
3.01	"	2.79	200
3.10	"	2.75	254
3.12	"	2.73	194
3.38	"	3.20	17
3.62	"	3.41	6
	3 hrs at 100°C		
1.55	"	1.51	480
1.62	"	1.65	472
1.88	"	1.70	137
2.02	"	1.80	98
2.20	"	1.92	spoiled
2.51	"	2.02	50
2.68	"	2.09	44
2.82	"	2.13	31
2.90	"	2.18	44
3.01	"	2.22	28
3.10	"	2.22	29
3.12	"	2.29	22
3.38	"	2.85	10
3.62	"	3.04	6
3.75	"	3.11	0

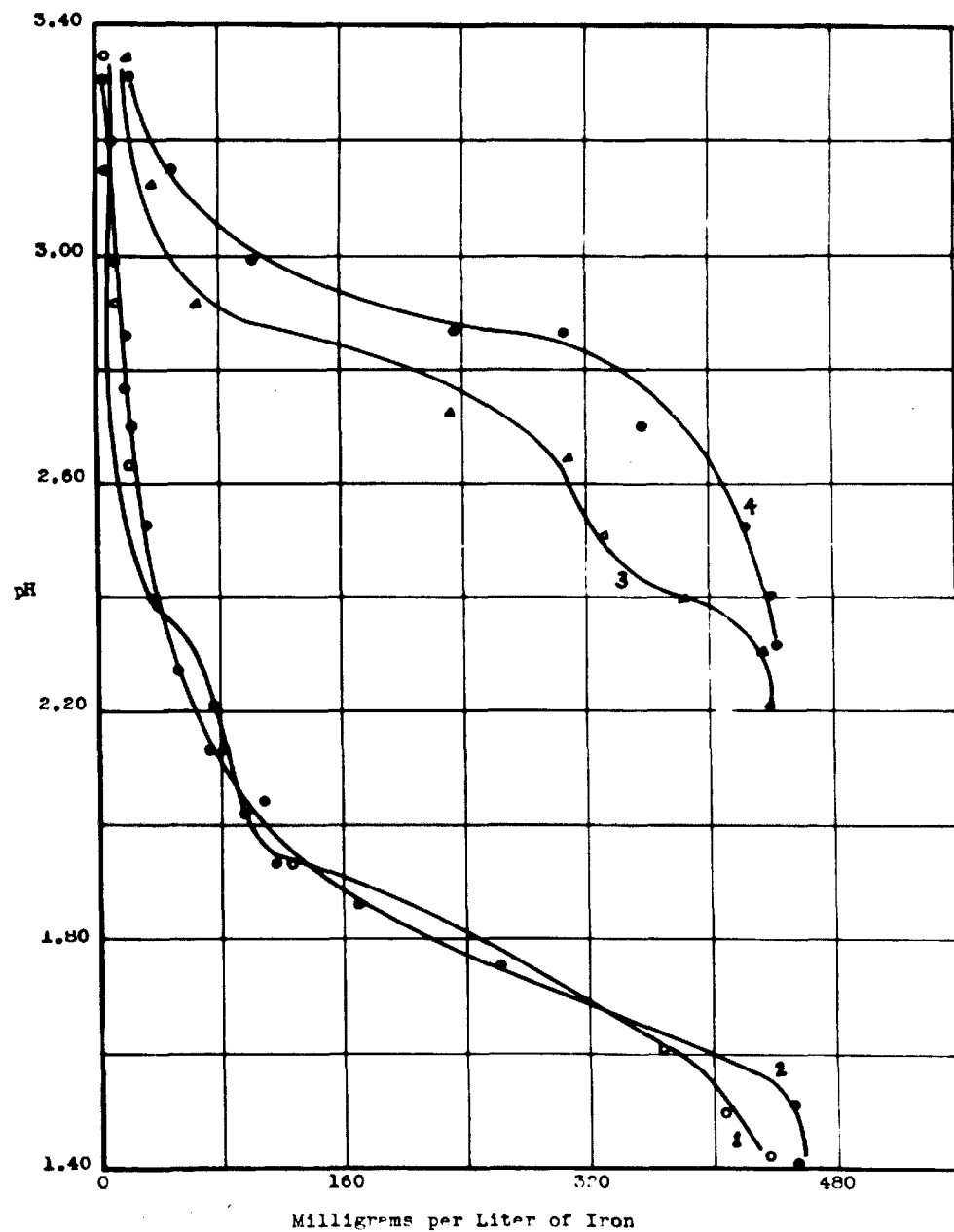


Fig. 14- Ferric iron in boric acid solution at different pH values:
 1, NH_4OH treatment, 3 hrs at 100°C .; 2, NaOH treatment, 3 hrs at 100°C .;
 3, NaOH treatment, 24 hrs at 26°C .; 4, NH_4OH treatment, 24 hrs at 21°C .

Removal of Ferric Iron from Boric Acid Solution

Table VII (c)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Fe^{3+} in soln.
(orig soln)	none	-	464
	24 hrs		
2.52	at 21°C	2.58	427
2.70	"	2.70	361
2.80	"	2.69	327
2.86	"	2.68	308
2.86	"	2.58	236
2.99	"	2.72	106
3.15	"	2.92	30
3.31	"	3.12	2
3.32	"	3.40	10
(orig soln)	none	-	463
	2 hrs		
	at 100°C		
1.38	"	1.32	464
1.50	"	1.48	412
1.63	"	1.64	341
1.74	"	1.69	267
1.85	"	1.72	173
1.92	"	1.72	119
2.02	"	1.62	112
2.12	"	1.66	74
2.26	"	1.82	56
2.52	"	1.87	34
2.70	"	1.86	25
2.86	"	1.82	20
2.99	"	2.25	14
3.15	"	2.45	6
3.31	"	2.55	3
3.32	"	2.68	2

Removal of Ferric Iron from Boric Acid Solution

Table VII (d)

pH after addition of NaOH	Treatment	pH after treatment	mg/l. Fe^{3+} in soln.
(orig soln)	none	-	440
	24 hrs at 26°C		
2.59	"	2.50	384
2.60	"	2.61	331
2.63	"	2.67	313
2.72	"	2.67	232
2.91	"	2.83	64
3.00	"	2.90	43
3.12	"	3.00	34
3.35	"	3.32	19
3.65	"	3.68	8
	3 hrs at 100°C		
1.48	"	1.52	408
1.60	"	1.64	349
1.78	"	1.64	140
1.92	"	1.70	129
2.01	"	1.75	97
2.12	"	1.75	84
2.20	"	1.74	76
2.39	"	1.80	37
2.63	"	1.91	21
2.72	"	1.95	23
2.77	"	1.98	20
2.91	"	2.28	14
3.00	"	2.38	9
3.12	"	2.48	7
3.35	"	2.71	6
3.65	"	2.82	4

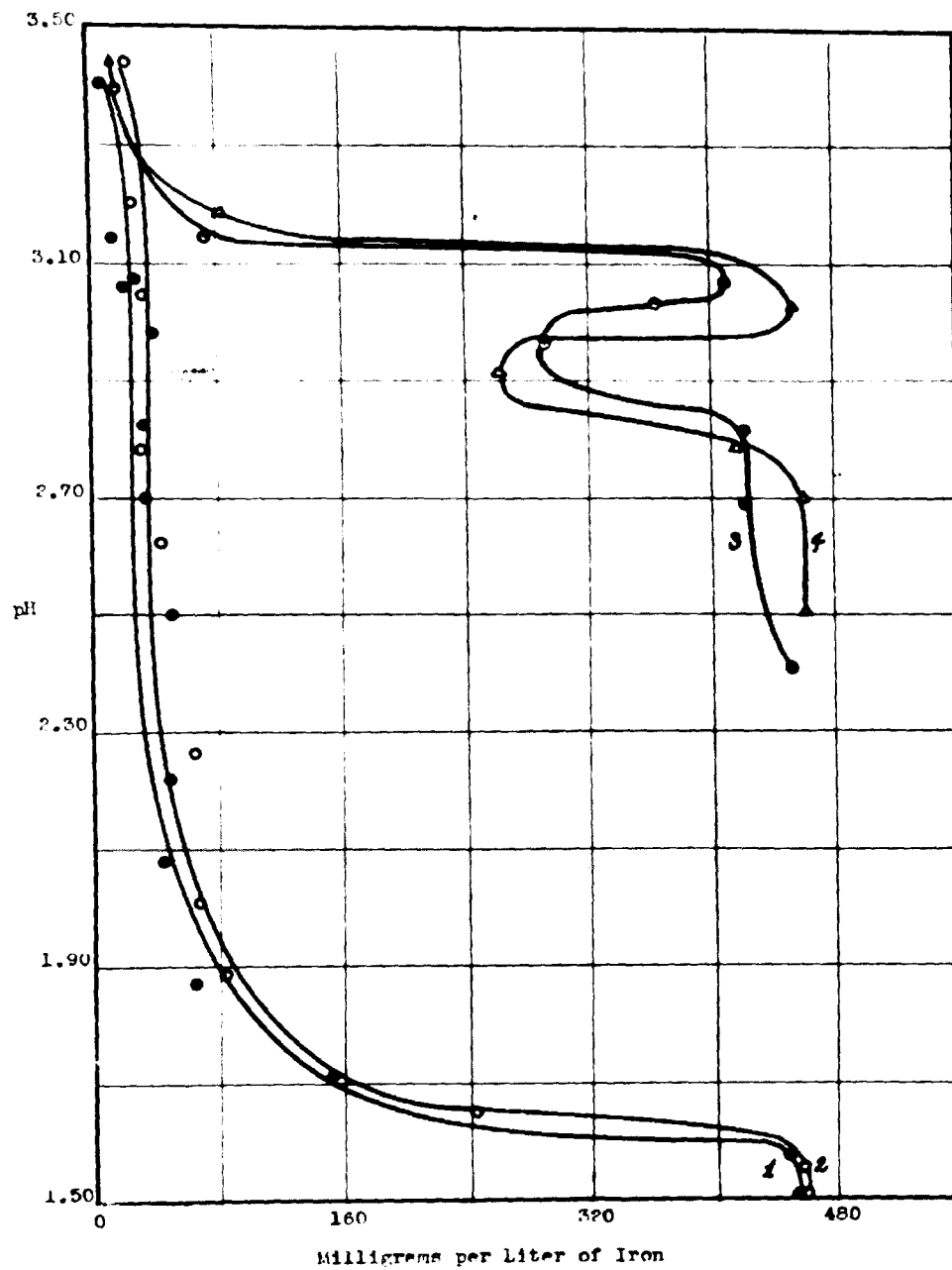


Fig. 15 - Ferric iron in buffered nickel sulfate solution at different pH values: 1, NaOH treatment, 3 hrs at 100°C.; 2, NH₄OH treatment, 3 hrs at 100°C.; 3, NaOH treatment, 24 hrs at 23°C.; 4, NH₄OH treatment, 24 hrs at 23°C.

Removal of Ferric Iron from
Buffered Nickel Sulfate Solution

Table VII (e)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Fe^{3+} in soln.
(orig soln)	none	-	460
	24 hrs at 50°C		
2.80	"	2.80	415
2.93	"	2.69	365
3.03	"	2.67	455
3.04	"	2.79	453
3.19	"	3.08	87
3.44	"	3.38	20
3.55	"	3.50	17
3.74	"	3.71	17
3.95	"	3.82	15
	5 hrs at 100°C		
1.56	"	1.62	455
1.67	"	1.62	249
1.72	"	1.63	69
1.89	"	1.73	87
2.01	"	1.78	71
2.14	"	1.85	49
2.27	"	1.92	69
2.63	"	2.04	42
2.80	"	2.10	29
2.93	"	2.15	39
3.03	"	2.18	20
3.04	"	2.43	28
3.12	"	2.74	25
3.45	"	2.95	23
3.55	"	3.00	25

Removal of Ferric Iron from
Buffered Nickel Sulfate Solution

Table VII (f)

pH after addition of NaOH	Treatment	pH after treatment	mg/l Fe in soln
(orig soln)	none	-	455
	24 hrs		
2.43	at 23°C	2.50	455
2.70	"	2.74	419
2.82	"	2.85	422
2.98	"	2.70	392
3.08	"	2.68	408
3.06	"	2.72	320
3.01	"	2.85	363
3.15	"	3.01	72
3.43	"	3.30	14
3.82	"	3.63	20
	3 hrs		
1.48	at 100°C	1.50	455
1.58	"	1.61	446
1.72	"	1.62	154
1.68	"	1.71	70
2.02	"	1.81	48
2.22	"	1.88	50
2.37	"	1.97	-
2.50	"	2.02	42
2.70	"	2.11	36
2.82	"	2.15	31
2.98	"	2.19	39
3.08	"	2.27	28
3.06	"	2.36	20
3.15	"	2.69	12
3.43	"	2.95	6
3.82	"	3.13	12

Summary of Data on Ferric Iron

Table VII (g)

Appearance of Turbidity

Solution	After addition of base		After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	3.4-3.5	3.2-3.5	2.7-2.8	2.5-2.6	1.5-1.6	1.5-1.6
H ₃ BO ₃	2.6-2.7	2.7-2.8	2.4-2.5	2.4-2.5	1.4-1.5	1.4-1.5
Buffered NiSO ₄	3.2-3.3	3.2-3.3	2.8-2.9	2.6-2.7	1.5-1.6	1.4-1.5

Heavy Precipitation

Solution	After addition of base		After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	above pH 3.5	above pH 3.4	above pH 3.1	above pH 3.2	above pH 1.9	above pH 1.8
H ₃ BO ₃	above pH 2.7	above pH 3.0	above pH 2.6	above pH 2.8	above pH 1.8	above pH 1.8
Buffered NiSO ₄	above pH 3.4	above pH 3.5	above pH 3.2	above pH 3.2	above pH 1.8	above pH 1.8

Removal of Ferric Iron

Solution	After 24 hrs at 22-27°C		After 3 hrs at 100°C	
	NaOH	NH ₄ OH	NaOH	NH ₄ OH
NiSO ₄	17 mg/l remain pH 3.4 6 mg/l remain pH 3.3	8 mg/l Fe ³⁺ remain pH 3.5	10 mg/l remain pH 3.4 Fe ³⁺ removed 3.3-3.7	28 mg/l remain pH 3.1 7 mg/l remain pH 3.5
H ₃ BO ₃	19 mg/l remain pH 3.4 8 mg/l remain pH 3.7	28 mg/l remain pH 3.3 10 mg/l remain pH 3.5	20 mg/l remain pH 3.8 8 mg/l remain pH 3.0	14 mg/l remain pH 3.0 3 mg/l remain pH 3.0
Buffered NiSO ₄	20 mg/l remain pH 3.2	20 mg/l remain pH 3.5 15 mg/l remain pH 3.3	20 mg/l remain pH 3.1 15 mg/l remain pH 3.6	25 mg/l remain pH 3.2 25 mg/l remain pH 3.6

Zinc:- Zinc was not appreciably removed from nickel sulfate solution with either ammonium or sodium hydroxide until a pH of 6.4 was reached, as may be seen from Fig. 16. Thereupon the curves break quite rapidly and with ammonium hydroxide the zinc is removed from solution completely at pH 6.8 after being heated for 3 hours at 100°C.

It was not possible to carry the precipitation with sodium hydroxide to a pH higher than 6.6 without considerable dilution of the zinc ion concentration.

Again in the case of the buffered nickel sulfate solution visual observations were of no value. Analyses showed that in the heated samples zinc was precipitated at a much lower pH in this solution than in nickel sulfate solution alone, but the possible effect of the precipitated nickel hydroxide must not be overlooked.

In carrying out the analysis, which was a combination of the separation method of Fales and Ware (19) and the polarographic procedure of Reed and Cummings (20), several points of importance should be noted and will be mentioned here: (1) In order to have sufficient zinc to work with conveniently at the lower concentrations fifty ml. samples were taken. (2) In the formic mixture, the use of either NH_4Cl or $(\text{NH}_4)_2\text{SO}_4$ were recommended, but for this case NH_4Cl was found preferable, since there was a large amount of nickel ammonium sulfate precipitated otherwise, as well as some zinc ammonium sulfate.

(3) It was essential that the solution be at pH 2.0 before saturating with hydrogen sulfide gas, otherwise nickel sulfide was precipitated and the zinc sulfide precipitation was incomplete. A small amount of nickel sulfide is not objectionable since the zinc sulfide may be dissolved in cold 1:1 HCl leaving the nickel sulfide.

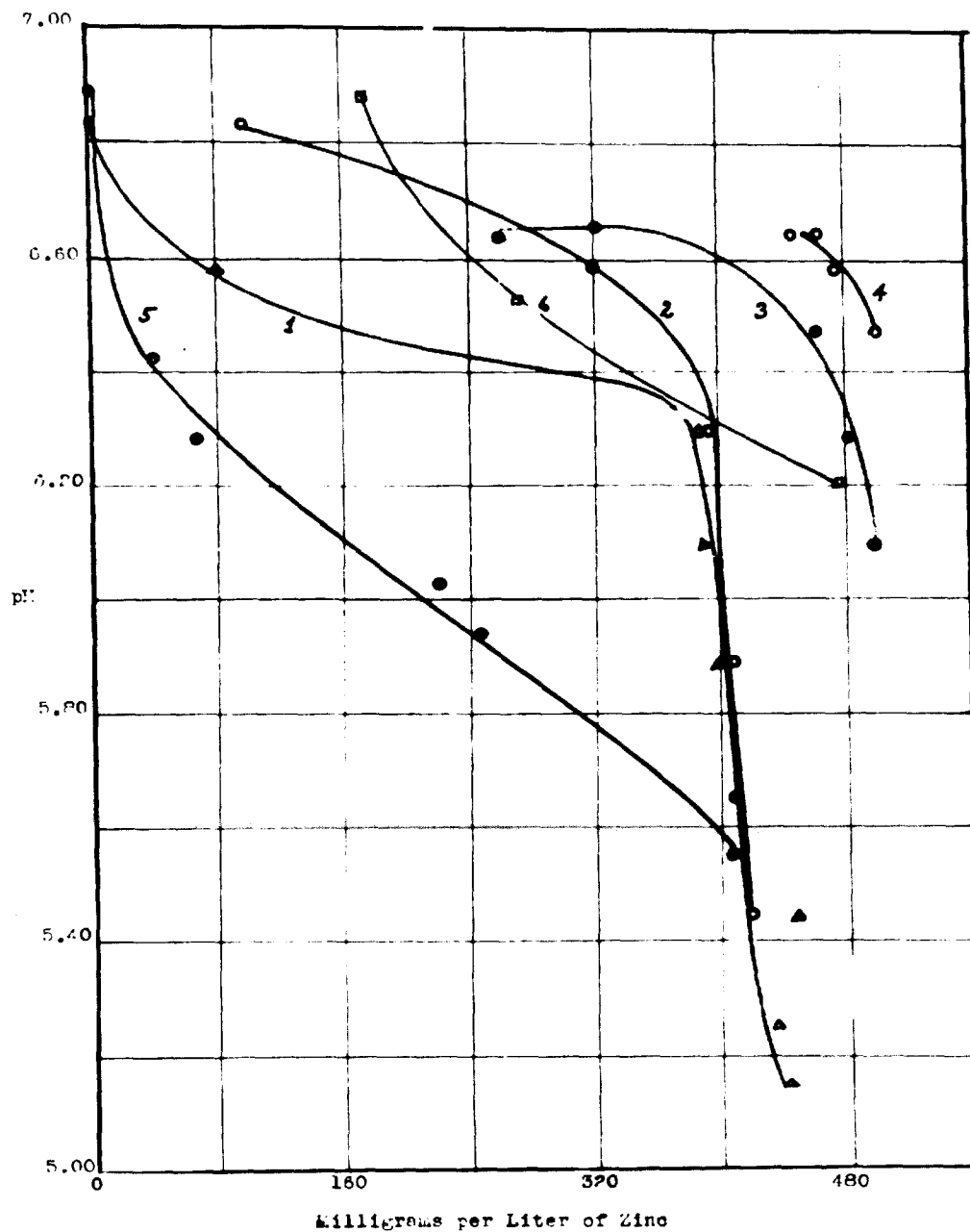


fig. 16 - Zinc in buffered and unbuffered nickel sulfate solution at different pH values: 1, Nickel sulfate solution after NH_4OH treatment, 3 hrs at 100°C .; 2, Nickel sulfate solution after NH_4OH treatment, 24 hrs at 26°C .; 3, Nickel sulfate solution after NaOH treatment, 3 hrs at 100°C .; 4, Nickel sulfate solution after NaOH treatment, 24 hrs at 22°C .; 5, Buffered nickel sulfate solution after NH_4OH treatment, 3 hrs at 100°C .; 6, Buffered nickel sulfate solution after NH_4OH treatment, 24 hrs at 25°C .

Removal of Zinc from Nickel Sulfate Solution

Table VIII (a)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Zn in soln.
(orig soln)	none	-	450
	24 hrs		
5.45	at 26°C	5.37	420
5.55	"	5.59	410
5.89	"	5.95	410
6.30	"	6.20	396
6.58	"	6.48	320
6.85	"	6.72	100
	3 hrs		
5.15	at 100°C	5.09	444
5.25	"	5.21	434
5.45	"	5.35	450
5.65	"	5.58	350?
5.89	"	5.81	400
6.10	"	6.02	390
6.30	"	6.21	390
6.58	"	6.38	80
6.85	"	6.67	0

Table VIII (b)

pH after addition of NaOH	Treatment	pH after treatment	mg/l. Zn in soln
(orig soln)	none	-	500
	24 hrs		
6.47	at 22°C	6.38	498
6.58	"	6.50	477
6.65	"	6.58	464
6.65	"	6.60	450
6.65	"	6.62	-
	3 hrs		
6.12	at 100°C	6.02	488
6.29	"	6.19	485
6.47	"	6.33	461
6.65	"	6.45	320
6.65	"	6.43	260
6.65	"	6.45	265

Removal of Zinc from
Buffered Nickel Sulfate Solution

Table VIII(c)

pH after addition of NH_4OH	Treatment	pH after treatment	mg/l. Zn in soln.
(orig soln)	none	-	432
	24 hrs		
6.17	at 25°C	6.29	477
6.53	"	6.67	273
6.93	"	7.01	173
	3 hrs		
5.55	at 100°C	5.45	407
5.73	"	5.55	spoiled
5.94	"	5.61	244
6.03	"	5.65	221
6.28	"	5.85	67
6.42	"	5.92	38
6.86	"	6.39	3

Mixture of Metallic Ions in Nickel Sulfate Solution:-

The results obtained with the mixture of metals were not entirely in agreement with those of the individual ions. Ferrous iron, for example, was reduced to a trace at a pH of 5.4 using ammonium hydroxide, whereas alone it was not removed at a pH of 6.8. This may be partially explained by the fact that oxidation occurred, as well as the possibility that some of it was adsorbed from solution by the hydrous aluminum oxide. Similarly, other discrepancies may be attributed to adsorption, or influence of other ions upon any single ion. The fact that results in this portion of the investigation are expressed qualitatively makes a comparison with the study of the individual metals difficult.

The symbols in Tables IX (a) and (b) are used according to the following scheme: P - ion present in approximately same concentration as in the original sample; p - ion present, but in a much lower concentration than the original; tr - a trace of the ion present; ab - ion removed from solution.

Mixture of Metallic Impurities in
Nickel Sulfate Solution

Table IX (a)

pH after NH ₄ OH addn	pH after 48 hrs at 25°C	Fe--		Al		Zn		Cu	
		48 hrs at 25°C	3 hrs at 100°C	48 hrs at 25°C	3 hrs at 100°C	48 hrs at 25°C	3 hrs at 100°C	48 hrs at 25°C	3 hrs at 100°C
4.90	4.62	p	p	ab	ab	P	P	P	P
5.40	4.78	tr	ab	"	"	P	P	P	P
5.82	5.10	ab	"	"	"	P	p	P	P
5.98	5.44	"	"	"	"	P	p	P	P
6.18	5.93	"	"	"	"	P	p	P	P
6.35	6.17	"	"	"	"	P	p	P	P
6.42	6.35	"	"	"	"	P	p	P	P
6.50	6.32	"	"	"	"	tr	ab	P	P
6.60	6.60	"	"	"	"	ab	"	P	P
6.75	6.73	"	"	"	"	"	"	P	P
6.93	6.93	"	"	"	"	"	"	p	ab
7.00	7.00	"	"	"	"	"	"	tr	tr
7.12	7.12	"	"	"	"	"	"	P	ab

Table IX (b)

pH after NaOH addn	pH after 24 hrs at 26°C	Fe++		Al		Zn		Cu	
		24 hrs at 26°C	3 hrs at 100°C	24 hrs at 26°C	3 hrs at 100°C	24 hrs at 26°C	3 hrs at 100°C	24 hrs at 26°C	3 hrs at 100°C
4.97	4.42	P	P	p	tr	P	P	P	P
5.25	4.39	P	P	p	tr	P	P	P	P
5.45	4.47	p	p	p	tr	P	P	P	P
5.80	4.41	tr	ab	tr	p	P	P	P	P
6.00	4.52	tr	"	tr	ab	P	P	P	P
6.42	4.54	ab	"	ab	"	P	p	P	P
6.65	5.05	"	"	"	"	p	p	p	p
6.80	5.28	"	"	"	"	p	tr	p	p
6.90	5.60	"	"	"	"	ab	ab	tr	ab

Treatment with NiCO_3 , Ca(OH)_2 and MgO :- Since NiCO_3 and Ca(OH)_2 are often used in purification of nickel plating baths it was thought desirable to determine the maximum pH values that could be obtained with buffered and unbuffered nickel sulfate solutions. Table X shows the results of this study. The data in Table X (a) were obtained upon treating nickel sulfate solutions with NiCO_3 , Ca(OH)_2 and MgO and allowing them to stand at 25 - 27°C with intermittent shaking.

It will be seen that in the unbuffered solution the pH was raised well above 6.0 with either NiCO_3 or Ca(OH)_2 . However, in the buffered nickel sulfate solution NiCO_3 failed to raise the pH to 6.0. Ca(OH)_2 did raise the pH above 6.0 in the unheated samples but only to pH 5.4 in the heated samples. The data indicate very definitely that the proper procedure to attain the maximum pH is to allow the NiCO_3 or Ca(OH)_2 to react with the buffered solution at room temperature. This is in accordance with the fact that the solubilities (27) of Ca(OH)_2 and NiCO_3 are much less at the higher temperatures. The heated series in Table X (b) was carried out by adding the NiCO_3 and Ca(OH)_2 at room temperature, then heating to 100°C and maintaining this temperature for 3 hours. When the solutions were heated to 100°C, the NiCO_3 and Ca(OH)_2 added, and the heating continued for 3 hours, the data in Table X (c) were obtained.

pH Values of Nickel Sulfate Solution (300 g/l)
Containing 1.8 g/l of NiCO_3 , Ca(OH)_2 and MgO

Table X (a)

	NiCO_3	Ca(OH)_2	MgO
Time	pH	pH	pH
1 hour	6.34	6.59	6.67
2 days	6.42	6.62	6.69
1 week	6.42	6.61	6.68

pH Values of Buffered and Unbuffered Nickel Sulfate
Solutions Treated with 5 g/l of NiCO_3 and Ca(OH)_2

Table X (b)

Solution	Subst. added	pH before treatment	Treatment	pH after treatment
NiSO_4	NiCO_3	2.89	6 hrs at 25°C	6.42
NiSO_4	NiCO_3	2.89	3 hrs at 100°C	6.52
NiSO_4	Ca(OH)_2	2.89	6 hrs at 25°C	6.71
NiSO_4	Ca(OH)_2	2.89	3 hrs at 100°C	6.63
Buffered NiSO_4	NiCO_3	2.70	6 hrs at 25°C	5.80
Buffered NiSO_4	NiCO_3	2.70	3 hrs at 100°C	5.22
Buffered NiSO_4	Ca(OH)_2	2.70	6 hrs at 25°C	6.30
Buffered NiSO_4	Ca(OH)_2	2.70	3 hrs at 100°C	5.40

Table X(c)

Solution	Subst. added	pH before treatment	Treatment	pH after treatment
NiSO_4	NiCO_3	3.18	3 hrs at 100°C	6.39
Buffered NiSO_4	NiCO_3	3.00	"	5.12
Buffered NiSO_4	Ca(OH)_2	2.97	"	6.58
Buffered NiSO_4	Ca(OH)_2	3.04	"	5.52

General Conclusions:- In general (with the notable exception of hexavalent chromium) initial precipitation, and precipitation after heating, occur at lower pH values from boric acid solutions than from buffered or unbuffered nickel sulfate solutions. Furthermore, the removal of impurities from buffered nickel sulfate starts at a lower pH than in the case of unbuffered nickel sulfate for heated solutions. As might be expected, more efficient removal of the impurities was effected in the solutions that were heated for 3 hours at 100°C, than in those that were allowed to stand at 22-27°C for 24 hours.

In the cases of aluminum, trivalent chromium, copper and ferric iron the hydrolysis process manifest itself in the heated samples in the form of a drop in pH amounting to 0.3-2.5 units.

Summary

1. The removal of aluminum, cadmium, trivalent and hexavalent chromium, copper, ferrous and ferric iron and zinc from buffered and unbuffered nickel sulfate have been studied at 22 - 27°C and at 100°C using ammonium hydroxide and sodium hydroxide whenever possible.
2. The removal of cadmium, trivalent and hexavalent chromium, copper, and ferric iron from boric acid solution was studied at 22 - 27°C and at 100°C using ammonium and sodium hydroxide.
3. The maximum pH values attained when buffered and

unbuffered nickel sulfate solutions were treated with 5 g./l. of NiCO_3 and Ca(OH)_2 and thoroughly stirred for 6 hours at 22 - 27°C or heated for 3 hours at 100°C were obtained.

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