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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISAANCE

The Precipitation of Chromic Hydrate From Chromic Chloride Solution

by

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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

The Precipitation of Chromic Hydrate From Chromic Chloride Solution

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ABSTRACT

Chromic hydrate has been precipitated in a readily filterable form at 60–80°C with high recovery of chromium by neutralising a solution of 0.8M chromic chloride in 2M hydrochloric acid, prepared by the reduction of a solution of 0.8M sodium chromate in 6M hydrochloric acid by methanol, with an aqueous suspension of 10 % w/v light magnesia. The precipitated chromic hydrate can be dried in air at 110°C to form a friable product that is suitable for use as an intermediate in the manufacture of anhydrous chromic chloride, and the magnesia is easily regenerated.

INTRODUCTION

Hydrated chromic oxide prepared by neutralising an aqueous solution of a chromium (III) salt, (1), is normally gelatinous in texture and slow filtering. In the present work conditions were investigated in which chromic hydrate might be precipitated in a readily filterable form of adequate purity for use as an intermediate in the commercial production of anhydrous chromic chloride by a low temperature chlorination process (2)(3). The chromic hydrate was precipitated from aqueous chromic chloride solution prepared by the reduction of a solution of sodium chromate in hydrochloric acid by methanol (4), using light magnesia as the base even though the hydration of lime is thermodynamically (5) more favourable, because lime cannot so easily be regenerated by the spray-roasting or steam hydrolysis of the chloride (6):

$$MgO(c) + H_2O(l) = Mg(OH)_2(c) \quad (\Delta H^\circ = -40.7 \text{ kJ mol}^{-1}; \; \Delta G^\circ = -30.4 \text{ kJ mol}^{-1})$$

$$CaO(c) + H_2O(l) = Ca(OH)_2(c) \quad (\Delta H^\circ = -65.2 \text{ kJ mol}^{-1}; \; \Delta G^\circ = -55.3 \text{ kJ mol}^{-1})$$

Ionic equilibria of aqueous Cr(III)

Three isomers of hexa-coordinated chromic chloride exist in equilibrium in aqueous solution (7)(8):

$$CrCl_2(H_2O)_4{}^+ + Cl^- + 2H_2O$$
(dark green)
$$\rightleftarrows CrCl(H_2O)_5{}^{2+} + 2Cl^- + H_2O$$
(bluish-green)
$$\rightleftarrows Cr(H_2O)_6{}^{3+} + 3\ Cl^-$$
(violet)

Concentrated acidic solutions containing chloride ions favour the dark green isomer, whereas the violet isomer predominates in dilute solutions of low acidity but is hydrolysed reversibly by hydroxyl ions. Excess hydroxyl ions precipitate mononuclear chromic oxide hydrate (9):

$$(Cr(H_2O)_6)Cl_3 \underset{HCl}{\overset{H_2O}{\rightleftarrows}} (Cr(OH)(H_2O)_5)Cl_2$$

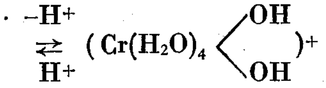
$$\underset{HCl}{\overset{H_2O}{\rightleftarrows}} (Cr(OH)_2(H_2O)_4)Cl \underset{HCl}{\overset{H_2O}{\rightleftarrows}} Cr(OH)_3(H_2O)_3$$

Slow addition of a dilute base to a well stirred solution of hexaquo chromic ions forms crystalline chromia bayerite, $Cr(OH)_3$, at about pH7, (10). A similar product can be precipitated at pH 10.5 by the controlled addition of 0.1 M $(CrNO_3)_3$ solution to 0.25M ammonia solution. If, however, a base is added rapidly to a freshly prepared solution of Cr(III) ions, a gelatinous greyish-blue form of chromic hydrate is precipitated; at a slightly slower rate of addition the precipitate is dark green and granular in appearance. Both products share the same indeterminate composition, $Cr_2O_3.xH_2O$, and are amorphous to x-rays. The differences in colour and texture have been attributed to particle size, the extent of aggregation and the amount of trapped water (8).

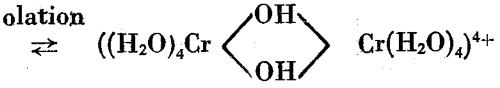
Condensation ploymers:

Olation: Hexaquo Cr(III) ions dimerise and trimerise very slowly in neutral solution to form *ol*-salts (8):

$$Cr(H_2O)_6{}^{3+} \underset{H+}{\overset{-H+}{\rightleftarrows}} (Cr(H_2O)_5OH)^{2+}$$



$$\overset{-H^+}{\underset{H^+}{\rightleftarrows}} \left(Cr(H_2O)_4 \langle {}^{OH}_{OH} \right)^+$$

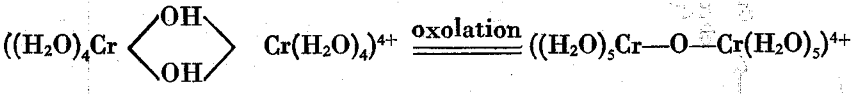


$$\overset{\text{olation}}{\rightleftarrows} \left((H_2O)_4Cr \langle {}^{OH}_{OH} \rangle Cr(H_2O)_4 \right)^{4+}$$

The rate of olation increases in basic solution with increase in temperature, Cr(III) concentration (11), and with anion (12) in the sequence: $CrCl_3 < Cr(NO_3)_3 < Cr_2(SO_4)_3$, but the reaction is severely inhibited in acidic solutions. Other soluble polycondensation products of $Cr(OH)_2(H_2O)_3$ are prepared by very slowly adding a base to an aged solution of Cr(III) ions in carefully controlled conditions (13).

At about pH 10.5 a dark green, macromolecular gel, amorphous to x-rays, can be precipitated (13) by neutralising a well stirred, dilute solution of $Cr(H_2O)_6^{3+}$ ions with aqueous ammonia over a period of 24 hours, or by the homogeneous *in situ* generation of ammonia in a solution of $Cr(NO_3)_3$ and urea simmered for about three hours. The *ol*-dimer, the soluble high polymers and the dark green gel may all have similar structures.

Oxolation: *Ol*-compounds also undergo further drastic and irreversible ageing over long periods of time or at elevated temperatures to yield soluble, inert, oxy-bridged compounds on standing in cold, dilute hydrochloric acid (14):



$$\left((H_2O)_4Cr \langle {}^{OH}_{OH} \rangle Cr(H_2O)_4 \right)^{4+} \overset{\text{oxolation}}{=\!=\!=\!=} \left((H_2O)_5Cr{-}O{-}Cr(H_2O)_5 \right)^{4+}$$

Thermal dehydration:

The slow precipitation reactions and thermal behaviour at low temperatures of freshly prepared aqueous $Cr(H_2O)_6^{3+}$ ions are summarised in Figure 1. When heated, amorphous chromic hydrate loses water over a wide range of temperature, depending on the nature of the atmosphere at high temperatures. Crystalline chromia bayerite slowly loses its crystallinity at 50 °C whether in an oxidising or non-oxidising atmosphere, or in aqueous solution, and becomes amorphous to x-rays with composition $Cr_2O_3 . \sim 3H_2O$ at about 100 °C. At higher temperatures the thermal behaviour of chromic hydrate is largely independent of the mode of preparation (10) (13) (15).

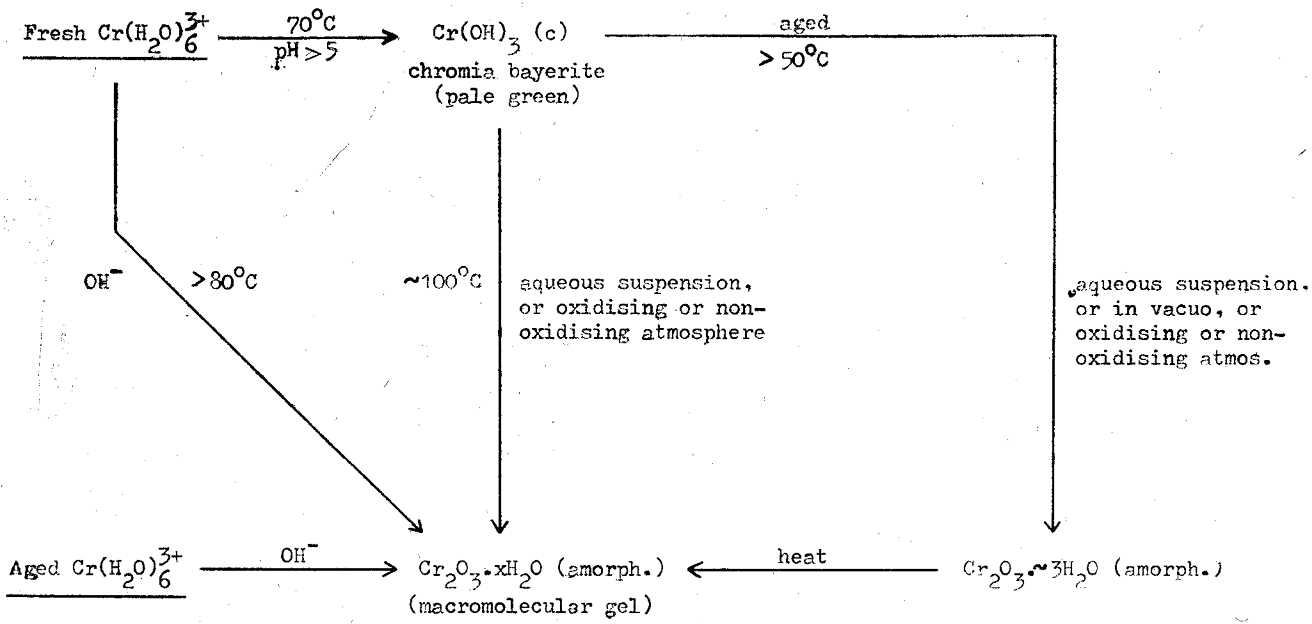


Figure 1. The slow precipitation reactions and low temperature thermal behaviour of chromic hydrate prepared from aqueous CrIII solution.

MATERIALS

'AnalaR' grade chemicals and G.P.R. light magnesium oxide were supplied by Hopkin and Williams Ltd. (16).

The light magnesia contained 54.6% Mg (equivalent to 90.6% MgO) as determined by EDTA titration, with 10.9% loss on ignition at about 700 °C; no barium impurity was detectable. A small endothermic TG-DTA peak at 317 °C corresponded with 5% loss in weight. The probable impurities were $Mg(OH)_2$ (17) and perhaps $MgCO_3$; natural brucite and natural magnesite decompose at 350 °C (18).

Owing to the micron-sized particles and low bulk density of light magnesium oxide (130–245 kg m^{-3}) (17) it was found convenient to use 10% w/v MgO in aqueous suspension. The apparent viscosity increased rapidly to a maximum value after an induction period of about 10 minutes, probably due to wetting and swelling of the porous particles as more than 90% of the surface area of magnesia is usually internal (17). The suspension was therefore aged for 20 minutes before use.

APPARATUS

Batch precipitations of chromic hydrate were carried out in reproducible, low shear rate mixing conditions that minimised the damage sustained by flocs, using a sinusoidal air-pulse generator running at 50 Hertz with 63 mm i.d. cylinder, 40 mm stroke length and a 25 mm i.d. sparge tube as the agitator.

ANALYTICAL PROCEDURE

A variety of analytical techniques were employed for the determination of elemental concentrations.

Na in solution: Flame emission spectrophotometry at 589.0 nm wavelength.

Mg and Cr in solution: Atomic absorption spectrophotometry at 285.2 and 357.9 nm respectively (19).

Cl in solution: Titration with 0.1M B.P. $AgNO_3$ solution at pH7 using K_2CrO_4 as an indicator.

Na in chromic hydrate: A sample was dissolved in the minimum amount of 2M HCl, diluted with distilled water and analysed by flame emission spectrophotometry as above.

Mg in chromic hydrate: Chromic hydrate was dissolved in the minimum amount of conc. HCl, diluted with distilled water to 200 ml and boiled. 15 ml of 300 gl^{-1} NH_4Cl was added; Cr was eliminated by boiling for 1 min, neutralising with ammonia and filtering hot. The precipitate was washed twice with hot 1.75% NH_4Cl solution, re-dissolved in hot 6M HCl, re-precipitated with 35% NH_3, filtered hot and washed three times with hot 1.75% NH_4Cl solution and once with hot distilled water. The filtrates and wash liquors were combined, evaporated down to 400 ml, filtered hot and the residual solid washed with hot distilled water; all the filtrates and wash liquors were combined and made up to 1 l, and titrated with EDTA solution using solochrome black as an indicator.

Cr in chromic hydrate: The chromic hydrate was dissolved in the minimum amount of 2M HNO_3, diluted with distilled water and analysed by atomic absorption spectrophotometry as previously described.

Cl in chromic hydrate: Chromic hydrate, dissolved in the minimum amount of 2M HNO_3 and treated with excess 10 g l^{-1} B.P. $AgNO_3$ solution, was acidified with 2M HNO_3 and allowed to coagulate in the dark. The precipitated AgCl was filtered and washed in a weighed, dry, sintered glass crucible and dried initially at 100 °C and then at 130 °C; the crucible was cooled in a darkened dessicator and weighed again.

EXPERIMENTAL PROCEDURE

Filtration tests

Simple vacuum filtration tests were carried out at 45 °C and 0.4 bar on a suspension of chromic hydrate that had been prepared at 80 °C and pH 5.85 by slowly adding 10% w/v light magnesia slurry in 5.9% stoichiometric excess to 0.860 l of a gently agitated solution of 0.804M chromic chloride in 1.98M hydrochloric acid, obtained by reducing a solution of 0.804M Na_2CrO_4 in 6.00M HCl with methanol (4). This was followed by further agitation for 20 minutes in order to encourage the hydrolysis and dissolution of magnesia.

0.25 l samples of the gently agitated slurry were withdrawn and replaced in turn with an equal volume of distilled water at 45 °C, thus diluting the slurry for each successive filtration test. Using a buchner funnel and Whatman No. 541 12.5 cm diameter hardened, ashless filter papers (mean dry weight: 0.98 ± 0.02 g) and controlling the pressure drop across the filter by means of an air-bleed valve, each sample was filtered and washed with 0.25 l of distilled water at ambient temperature with 25 s dry time allowed in each case. Cake form times and mean flow rates of filtrate and wash liquor were measured. The filter cake thickness, net weight of cake and loss on ignition at about 700 °C were determined.

Metallurgical balance

Batch A: 0.860 l of a gently agitated solution of 0.804M $CrCl_3$ in 1.98M HCl (prepared as above) was precipitated at 80 °C and pH 6.85 by the slow addition of 10% w/v light magnesia in 5.9% stoichiometric excess, followed by further agitation for 20 min. The precipitate was filtered at 42 °C, washed with water (1 l at ambient temperature), weighed, dried for 5 h at 110 °C and re-weighed. The filtrate and wash liquor were then analysed for Na, Mg and Cr, and the dried product was analysed for Na, Mg, Cr and Cl content.

Batch B: In a complementary experiment a similar batch of precipitated chromic hydrate was filtered at 62 °C and washed with 1 l of distilled water at ambient temperature. Analyses were performed on the product (dried for 5 h at 110 °C), the filtrate and the wash liquor.

RESULTS AND DISCUSSION

Ammonia-precipitated chromic hydrate

Ammonia-precipitated chromic hydrate was selected as a reference material for the relative ease with which it can be washed free of the likely impurities, all of which are soluble.

Chromic hydrate precipitated by the dropwise addition of (i) 1.4%, (ii) 7.0% and (iii) 17.5% ammonia solution to 0.45M chromic chloride solution was observed to be, respectively, (i) pale green, (ii) blue and flocculated, and (iii) bluish-green and flocculated with a small proportion of dark green, granular particles. All the precipitates were gelatinous and difficult to filter. Boiling the suspension for 2 min promoted flocculation without improving the filtration characteristics but subsequent washing of the precipitate with distilled water inhibited the effect, presumably by removing residual chloride electrolyte from the system (8). Boiling also caused the blue precipitate gradually to become dark green and granular, which is attributable to a small degree of olation with consequent changes in the size and water content of the constituent particles.

Ageing: The pale green precipitate was thermally unstable, turning blue upon being dried for 2 h at 110 °C, and so resembled chromia bayerite (10). Certainly the conditions in which the precipitate was obtained were conducive to a low rate of nucleation relative to rate of crystal growth according to the theory of homogeneous precipitation (20), which can be represented as a first approximation by the following equations:

rate of nucleation = $K_1\exp(-K_2/(\ln S)^2)$

rate of crystal growth = $K_3(S-1)$.

where: K_1, K_2, K_3 = constants of proportionality

S = supersaturation ratio

= (bulk concn. - solubility) /(solubility)

Thus the slow addition of dilute ammonia solution tends to promote the growth of ordered crystals, whereas the rapid nucleation of gelatinous, amorphous chromic hydrate is favoured by high supersaturation ratios. When vigorously stirred solutions of 0.02–0.05M $CrCl_3$ and 0.0–0.8M NH_4Cl in 0.4–0.6M HCl were neutralised by the cautious dropwise addition of 35% NH_3 solution, a deep purple sol of chromic hydrate, stable for 24 h, was formed at about pH6 when the concentration ratio [Cl total] : [Cr] exceeded 124: 1. At these high ionic concentrations electrical effects are swamped and so modern colloid theory cannot satisfactorily explain the phenomenon; the cause remains obscure.

Stoichiometry:

35% NH_3 solution was slowly added to a gently agitated solution of 0.513 kg of $CrCl_3.6H_2O$ in 1.56 l of distilled water. It was found that the molar ratio of ammonia (added): chromic chloride (initially present) was 2.97: 1 at pH 7.00, which is in close agreement with the theoretical stoichiometric equation:

$$2CrCl_3(aq) + 2\ NH_3(aq) + (x + 3)\ H_2O(l)$$
$$= Cr_2O_3 . xH_2O(amorph.) + 6\ NH_4Cl(aq)$$

The solubility of Cr^{3+} ions at pH7 derived from the mean solubility constant (21) and thermodynamic data (5) is 3×10^{-4} ppm, as shown in Figure 2.

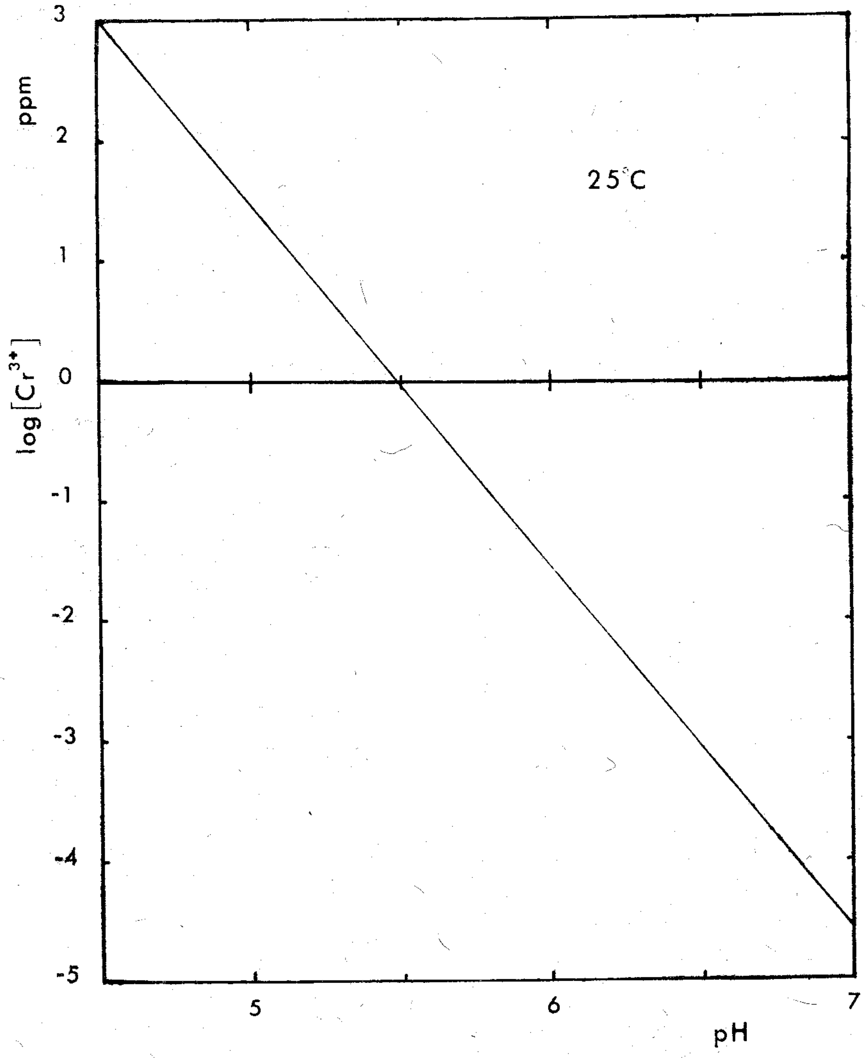


Figure 2. Log (solubility of Cr^{3+}) vs. pH of solution.

Excess reagents:

The presence of hydrochloric acid and methanol as excess reagents in the reduction of a solution of sodium chromate in hydrochloric acid by methanol (4), had no apparent effect on the precipitation of chromic hydrate from aqueous chromic chloride beyond the stoichiometric requirements for the neutralisation of the excess hydrochloric acid. Excess sodium chromate, on the other hand, caused the chromic hydrate to be precipitated in a brown, gelatinous form.

In order to assess the stoichiometric effect of excess sodium chromate, a solution of 0.28g of Na_2CrO_4 and 0.34 g of $CrCl_3.6H_2O$ in 30 ml of 0.5M HCl was neutralised with dilute NH_3 solution, filtered, washed carefully with distilled water and ignited at about 700 °C. The weight of yellowish-green residue after ignition exceeded the theoretical weight according to the stoichiometric equations for precipitation (above) and thermal dehydration (below) by 36%:

$$Cr_2O_3.xH_2O(amorph.) = Cr_2O_3(c) + xH_2O(g)$$

This was attributed to the presence of chromic chromate in the precipitate (8) (22).

Light magnesia

The pH of 100 ml of a suspension of 10% w/v light magnesia in distilled water, boiled for 10 min to encourage hydration, stirred and measured after 1 h, 24 h and again after vigorous stirring, was found to be pH 11.3, pH 10.3 and pH 10.7 respectively. The measured pH after standing for 24 h was similar to the equilibrium value obtained in a previous study (pH 10.38, experimental value) (17) and the theoretical value, pH 10.36, derived from the published mean solubility constant (5). Earlier research (17) had indicated that the rate of surface hydration (4% w/v MgO, 9-38 °C, turbulent conditions) appeared to be very rapid and the rate of nucleation of $Mg(OH)_2$ in a locally supersaturated solution extremely rapid, suggesting that the rate controlling step in the hydrolysis and dissolution of magnesia is probably the removal of Mg^{2+} and OH^- ions from the surface (activation energy, 57.7 kJ mol^{-1}). The slow rate at which the equilibrium pH was approached after stirring in the present work with a less turbulent system, however, suggests that the nucleation of $Mg(OH)_2$ can be a slow step in the hydration process.

Magnesia-precipitated chromic hydrate

Using knowledge of the ammonia-precipitation system as a basis, conditions favourable for the precipitation of chromic hydrate from chromic chloride solution with 10% w/v light magnesia were investigated semi-quantitatively. The use of 1.0M $CrCl_3$ solution was found to result in an excessively viscous slurry after precipitation and so 0.8M $CrCl_3$ was preferred in the present work.

Temperature:

The effect of temperature in the range 22–100 °C on the appearance of chromic hydrate precipitated from 0.8M $CrCl_3$ solution prepared by the reduction of 0.167 l of 0.8 M Na_2CrO_4 in 6.0M HCl with 5 ml of MeOH is indicated in Table 1; all of the precipitates filtered more readily than the corresponding ammonia-precipitates, especially at 75–80 °C.

Table 1. The effect of precipitation temperature on the appearance of MgO-precipitated chromic hydrate.

Temperature °C	Appearance of precipitate
22	blue flocs
50–52	blue flocs
75	bluish-green flocs
80	greenish-blue flocs
100	dark green, granular

Upon being dried in air for 24 h at 110 °C the blue magnesia-precipitated chromic hydrate turned greenish-blue but reverted to the blue state after standing in air for 1 week. Washing with dilute HCl (pH5) before filtration stabilised the dark green precipitate: blue, acid-washed chromic hydrate, converted to the dark green form by air drying for 4 h at 110 °C, remained greenish-blue on standing in air for as long as 1 year. This accords with reported observations that the rate of ageing of chromic hydrate increases (8) in a medium with a slight solvent action.

The blue chromic hydrate dried readily in air at 110 °C to form a porous, friable product, whereas the dark green, granular precipitate was very slow drying and formed a coarse, hard, granular product. The present work was therefore carried out with freshly precipitated blue chromic hydrate prepared at 60–80 °C and washed at ambient temperature with distilled water.

Flocculating agents:

Dow 'Separan' NP10 polyacrylamide solution was found to be an effective flocculating agent for precipitated chromic hydrate but the flocs were insufficiently strong for the filtration characteristics of the suspension to be significantly improved.

Excess reagents:

As with NH_3-precipitated chromic hydrate, the presence of excess methanol and hydrochloric acid had no discernible effect on the precipitation of chromic hydrate with magnesia. Sodium chromate, however, resulted in the precipitation of a brownish-green, gelatinous product at pH6 that was not readily filterable. Chromic chloride solutions prepared in the present work by the reduction of a solution of Na_2CrO_4 in HCl by methanol (4) were tested before use for the presence of excess Na_2CrO_4 by neutralising a sample of the $CrCl_3$ solution with dilute NH_3 solution, filtering out the precipitated chromic hydrate and confirming that the filtrate was colourless and thus not contaminated with yellow CrVI ions.

Filtration tests

The results of the filtration tests given in Tables 2 and 3 indicate filtration rates estimated on the basis of an industrial rotary drum vacuum filter with 25 % active filtration area. Results in the range 8.8–12.4 kg $m^{-2}h^{-1}$ on a Cr-basis compare favourably with previously reported filtration rates (1) of 6–12 kg $m^{-2}h^{-1}$ for unconditioned chromic hydrate precipitated at 90 °C with magnesia from mixed chloride liquors containing 10–29 g l^{-1} of Cr along with various amounts of Ni, Fe, Co and

Table 2. Chromic hydrate filtration tests: filtrate and wash liquor flow rates.

Filtration test	Concn. of Cr in feed	Filtrate				Wash liquor			
	gl^{-1}	Form time s	Dry time s	Volume l	Mean flow rate ml s^{-1}	Form time s	Dry time s	Volume l	Mean flow rate ml s^{-1}
1	26.4	39	20	0.193	3.27	33	20	0.255	2.98
2	18.9	30	20	0.210	4.25	41	20	0.252	5.58
3	14.0	24	20	0.215	4.89	37	20	0.251	4.40
4	12.0	25	20	0.220	4.89	22	20	0.249	5.66

Table 3. Chromic hydrate filtration tests: cake production rates.

Filtration test	Washed filter cake			
	Cake thickness mm	Net weight of cake g	Loss on ignition %	Cake production rate (Cr-basis) kg m^{-2} h^{-1}
1	4.0	62.05	84.4	12.4
2	3.2	49.37	85.9	11.5
3	2.8	36.39	86.0	10.7
4	2.7	30.97	86.3	8.8

Mo. Precipitation with lime or calcium carbonate usually leads to lower filtration rates (2.6–10.7 kg $m^{-2}h^{-1}$) but a rate of 25.3 kg $m^{-2}h^{-1}$ has been obtained using a kieselguhr precoat. Hygrothermal treatment of MgO-precipitates for 1h at 120 °C aid 1h at 200 °C has been shown to be effective in increasing filtration rates to 25 and 65 kg $m^{-2}h^{-1}$ respectively but the savings that can be obtained by using smaller filters are outweighed (1) by the costs of the hygrothermal treatment.

Metallurgical balance

The analytical data for Batch A presented in Table 4 form the basis for the metallurgical balance described in Figure 3. The results are in good agreement with the following three theoretical stoichiometric equations:

$$2CrCl_3(aq) + 3Mg(OH)_2(aq) + (x-3)\ H_2O(1)$$

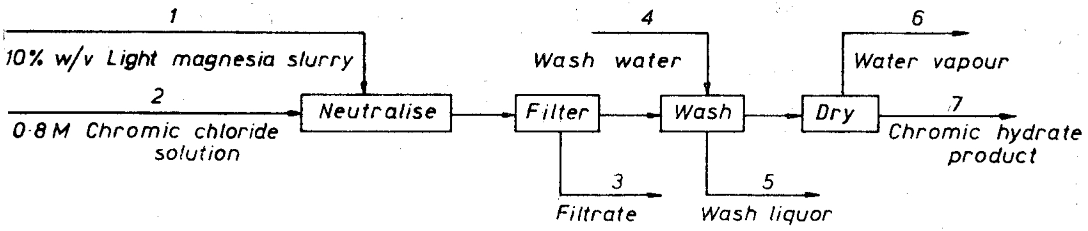
$$= Cr_2O_3 . xH_2O\ (amorph.) + 3MgCl_2(aq)$$

$$Mg(OH)_2(aq) + 2HCl(aq) = MgCl_2(aq) + 2H_2O(1)$$

$$MgO(s) + H_2O(1) = Mg(OH)_2(1)$$

The experimentally determined molar ratio, Mg: Cr, corresponding with the first equation after discounting the amount of magnesia consumed according to the second equation, was found to be 1.48: 1, and the concentration of chromium in the filtrate and wash liquor was of a low order of magnitude as predicted by thermodynamics and solubility theory (5) (21).

It will be noted that both aqueous chromic chloride and excess hydrochloric acid react with magnesia to form aqueous magnesium ions. The pH at which the solubility product (5) of $Mg(OH)_2$ is exceeded is therefore a function of the initial concentrations of H^+ and Cr^{3+} ions as shown in Figure 4; this, in conjunction with an arbitrary choice of ac-



Stream / Metal	1	2	3	4	5	6	7
Na g(± 3%)	—	31·8	29·0	—	1·80	—	1·20
Mg g(± 3%)	45·6	—	32·3	—	12·4	—	2·24
Cr g(± 3%)	—	35·9	7·3mg	—	0·6mg	—	35·6

Figure 3. Metallurgical balance.

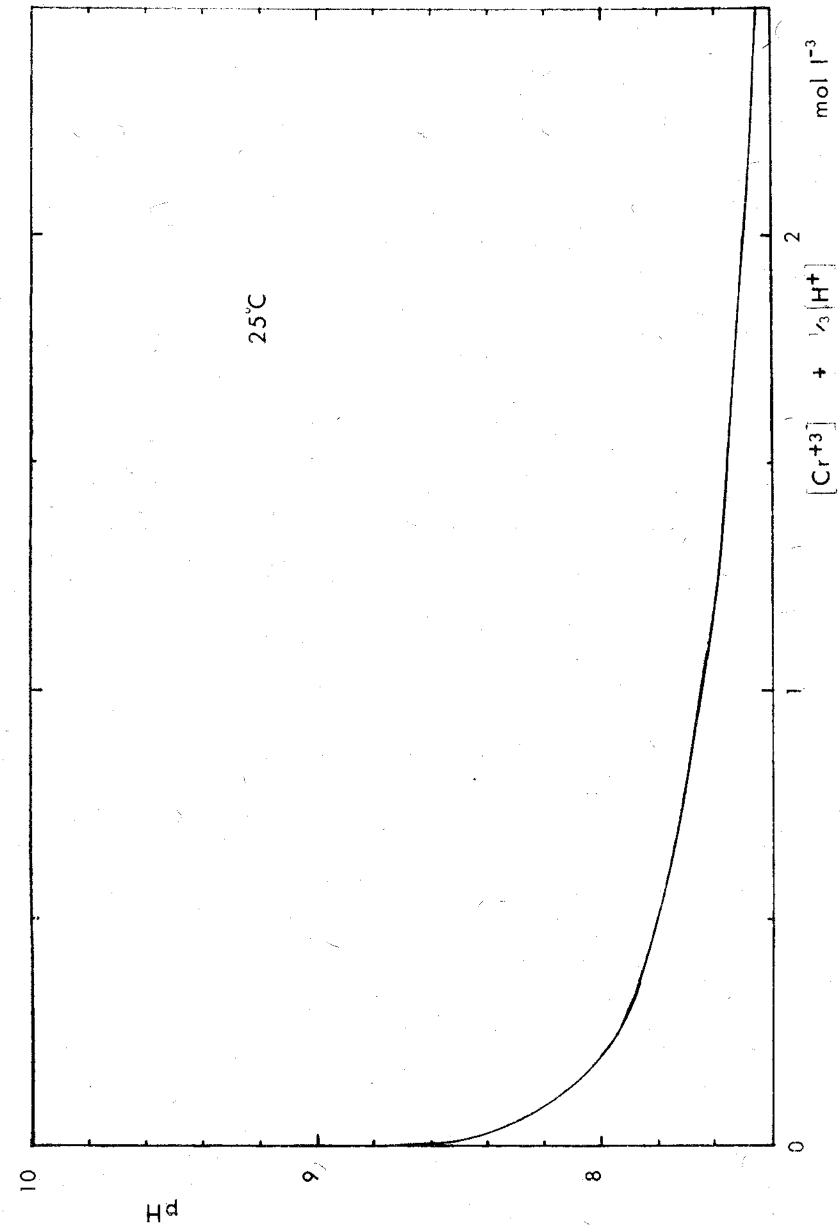


Figure 4. pH of solution at saturation with respect to $Mg(OH)_3$ vs. initial concentration of Cr^{3+} and H^{+}.

ceptable Cr^{3+} solubility, say 1 ppm (see Figure 2), provides the lower and upper pH-constraints for the magnesia precipitation system.

Regeneration of magnesia

The analyses of Batch B (Table 4) suggest that the filtration and wash liquors obtained from the light magnesia precipitation process would probably be amenable to an already developed process (24) for the regeneration of waste hydrochloric acid streams containing, for example, 8.9% $MgCl_2$ and 5.6% NaCl, in which sodium chloride is completely precipitated by evaporation under vacuum to 35% $MgCl_2$; hydrous magnesium chloride is recovered by further evaporation to 50% $MgCl_2$ with submerged burners. Solid hydrous magnesium chloride can be hyd-

Table 4. Batch tests: analyses.

Sample	Analysis		Batch test	
			A	B
Dried chromic hydrate	Na,	%	0.70	0.051
	Mg,	%	1.32	1.14
	Cr,	%	20.9	
	Cl,	%	3.44	
	weight,	g	170	
	loss on ignition,	%	67.5	46.7
Washed filter cake	weight,	g	490	
	loss on drying,	%	75.5	79.4
Filtrate	Na,	g l^{-1}	24.0	15.3 (15)
	Mg,	g l^{-1}	26.7	22.8 (21)
	Cr,	mg l^{-1}	6.0 [5.6]	9
	Cl,	g l^{-1}		98.6
	density,	g ml^{-1}	1.103	1.097
	total dry solids,	g l^{-1}		270
	per cent saturated,	%		50
	volume,	l	1.21	1.17
Wash liquor	Na,	g l^{-1}	1.7	6.6 (7)
	Mg,	g l^{-1}	11.7	13.1 (12)
	Cr,	mg l^{-1}	0.6 [0.6]	4
	Cl,	g l^{-1}		49.3
	density,	g ml^{-1}	1.043	1.043
	total dry solids,	g l^{-1}		128
	per cent saturated,	%		20
	volume,	l	1.06	

Note: Confirmatory data in parentheses:
( ) – atomic absorption spectrophotometry
[ ] – ditto (using the method of additions)

rolysed at 500 °C (25) with a steam-air mixture, or the aqueous solution can be spray-roasted. The regenerated magnesia thus obtained would be relatively active (26)(27) owing to the low temperatures employed (typical spray-roasting temperatures: reaction zone, 600–750 °C; outlet zone, 300–400 °C).

The use of ammonia rather than magnesia as a base would clearly be less economical for the commercial production of chromic hydrate as its regeneration involves the regeneration of magnesia also (6):

$$2NH_4Cl + Mg(OH)_2 \overset{H_2O}{=\!=} MgCl_2.H_2O + 2NH_3(aq)$$

$$MgCl_2.H_2O \overset{200\,°C}{=\!=\!=} MgO.HCl + HCl$$

$$MgO.HCl \overset{550\,°C}{=\!=\!=} MgO + HCl$$

Overall: $$NH_4Cl =\!=\!= NH_3 + HCl$$

CONCLUSIONS

Chromic hydrate can be precipitated with high recovery of chromium by the neutralisation with an aqueous suspension of light magnesia of a solution of chromic chloride prepared by the reduction (4) of a solution of sodium chromate in hydrochloric acid by methanol, in accordance with the stoichiometric equation:

$$2CrCl_3(aq) + 3MgO + xH_2O(l) = Cr_2O_3.xH_2O(amorph.) + 3MgCl_2(aq)$$

The molar ratio Mg: Cr determined at pH 6.85 was found to be 1.48: 1, net of the amount of magnesia consumed according to the stoichiometric equation:

$$MgO(s) + 2HCl(aq) = MgCl_2(aq) + H_2O(l)$$

In the absence of unreduced CrVI, and provided that the pH and stoichiometric quantities are carefully controlled, a readily filterable form of chromic hydrate of satisfactory purity for use as an intermediate in the manufacture (2) (3) of anhydrous chromic chloride can be prepared with 10% w/v light magnesia at 60–80 °C. The concentration of chromium remaining in solution after precipitation at pH 5.75 and pH 6.85 respectively was found to be 9 and 6 ppm. The magnesia could easily be recovered by means of the well known processes of spray-roasting or steam-air hydrolysis.

Later publications will describe the characteristics of the MgO-precipitated chromic hydrate and its reactivity towards a chloridising environment.

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ÖZET

Ağırlıkça % 10 magnezya içeren sulu süspansiyon ve metanos kullanılarak, GM hidroklorik asitteki 0.8 M kromat çözeltisinin indirgenmesi ile hazırlanmış olan krom (III) klorünün 2 M hidroklorik asitteki çözeltisinden, nötralizasyon yoluyla, kromun geniş ölçüde geri kazamemasına olanak sağlayan ve 60-80° C sıcaklıklarda kolaylıkla süzülebilen krom (III) hidrat çöktürülebilmiştir, Çöktürülen krom (III) hidrat havada 110° C de kurutulabilmiştir. Gevrek bir yapıya sahip olan ürün, susuz krom (III) klorüdün elde edilmesinde ara madde olarak kullanılabilmekte ve magnezyanın rejénerasyona da kolaylıkla gerçekleştirilebilmektedir.

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