COMMERCIAL EXTRACTION TECHNOLOGY AND PROCESS WASTE DISPOSAL IN THE MANUFACTURE OF CHROMIUM CHEMICALS FROM ORE

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1. Introduction

The element chromium was isolated by Vauquelin(Glenn, 1895) around 1797 from the mineral crocoite (lead chromate) discovered in 1765 by a Russian geologist Pallas, in a mine near Ekaterinburg(Mutual Chemical Company, 1941).The mineral chromite was discovered in the same area in 1798 and has always generally been the exclusive primary source of chromium for the metallurgical, chemical and refractory industries. Estimated world annual consumption is around 12.5 million tonnes of which approximately 85% is consumed by metallurgy, 8% by chemicals and 7% by refractories(International Chromium Development Association, 1999).

Chromite refers to the mineral (Mg, Fe) (Al, Cr, Fe)$_2$O$_4$ in which the chromic oxide content varies typically between 15 and 65%; iron exists in both di and trivalent states; minor compounds of significance are silicates and oxides of vanadium. Not all chromites are true spinels; some are a mixture of spinel and corundum oxides (Cr_2O_3, Fe_2O_3). The challenge for the chromium chemicals industry has always been to find the most effective way of using available raw materials to convert the chromium contained in this relatively unreactive mineral into a range of products of the purity required by user industries. Commercial production is via sodium chromate or more typically via the dichromate to give the range of hexavalent or trivalent chromium compounds.

2. Commercial process evolution

Commercial production of chromium chemicals from ore began in the UK and USA in 1810–25 and involved 'the opening up of the ore with soda and lime and

further application of the roast product have been learned, so that there have been developed whole processes that leave little to be desired in method or use' (Udy, 1956). Table 1 summarises process evolution.

TABLE I

Sodium dichromate process evolution

Generation	1st	2nd	3rd	4th	5th
Process flow	Batch	Batch	Continuous	Continuous	Continuous
Process type	Lime	Lime	Lime	No lime	No lime
Kiln size kT/y	<1000	5000	10000	20000	75000
Introduced UK	Pre 1920	1930–1940	1950's	1960's	1980's

The first processes used potassium nitrate and produced potassium chromate. Nitrate was replaced by carbonate around 1820 and potassium by sodium around 1880. A very significant development in 1845 was the discovery that addition of lime improved oxidation of the chromium by preventing the reacting mix from fusing. In turn, lime was replaced by cheaper limestone or dolomite. Addition of lime had several process advantages: efficient extraction of a wide range of ore qualities; minimised negative effects of silicates; immobilised vanadium. Lime-based processes remained exclusive as operations developed in technique and scale until the late 1950's/early 1960's when lime-free alternatives began to be developed.

Today virtually all producers outside Eastern Europe, the former Soviet Union, India, Pakistan and China use lime-free extraction processes, accounting for around 60% of global capacity (Table II). Ore geochemistry dictates, principally via crystallographic phases present together with magnesium and silica contents, whether or not lime-free technology can be applied successfully. Figure 1 – a modified Pourbaix Eh/pH diagram(Pourbaix, 1974), represents key reactions in the manufacture and use of chromium chemicals.

Apart from inclusion/exclusion of lime, details of the extraction process have not changed. It was, and still is, based on high temperature alkaline oxidation with the preferred alkali metal source being sodium carbonate or, to a much lesser extent, sodium hydroxide.

The numbers by the arrows in Figure 1 refer to various chromium species conversions:

1. Chromic oxide to chromium metal.
2. Trivalent chromium in ore to chromate.
3. Chromate to dichromate.
4. Dichromate to chromic acid.
5. Dichromate to chromic oxide.
6. Dichromate to for example, basic chromium sulphate.

TABLE II

Estimated world production of sodium dichromate as kT/y $Na_2Cr_2O_72H_2O$

	1948	2000	Process type
Argentina	–	25	N.L.
Australia	3.0	–	
Belgium	1.2	–	
Brazil	0.3	–	
China	?	90	H.L.
France	4.4	–	
Germany	7.5	–	
India	2.9	(a)	
Italy	3.0	(a)	
Japan	8.0	50	N.L.
Kazakhstan	?	80	H.L.
Russia	?	40	H.L.
South Africa	5	65	N.L.
Turkey	–	40	N.L.
UK	13	125	N.L.
USA	87	145	N.L/V.L.L.
Others		80(b)	Mainly H.L.
Total	∼ 140	740	

1948: numbers taken from Udy (1956), all high-lime processes; 2000: numbers are Elementis Estimates (Elementis, 2000); (a): numbers included in 'others' (b); N.L.: no lime; H.L.: high lime; V.L.L: very low lime.
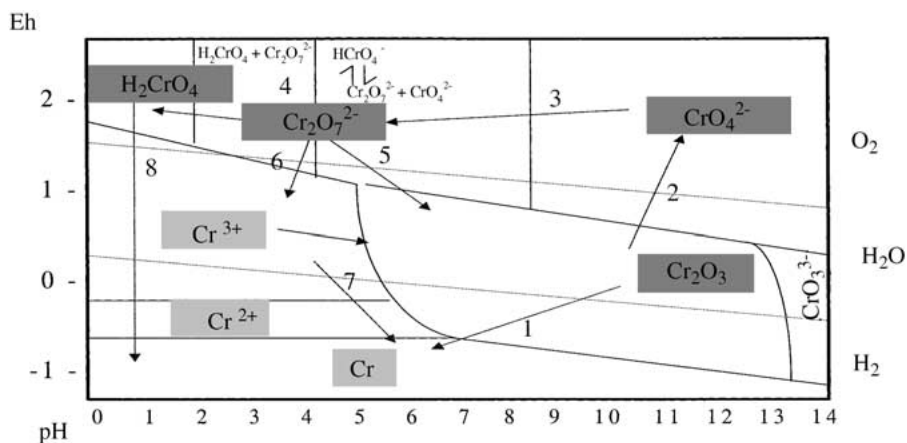

Figure 1. A modified Pourbaix Eh/pH diagram (Pourbaix, 1974) representation of the manufacture and use cycle of chromium chemicals. Although this indicates that aqueous phase oxidation occurs, it does so slowly in the case of chromite as to be of no commercial significance.

7. Soluble trivalent chromium to metal by electrolysis.
8. Chromic acid to metal by electrolysis.

The method employed enables chromium to be separated from most other components of the ore in a single operation followed by some relatively simple stages to control levels of impurities such as alumina and vanadium. Other techniques involving selective chlorination or via ferrochromium are unable to provide economically the range of products (Figure 2) at the purity required by modern user industries.
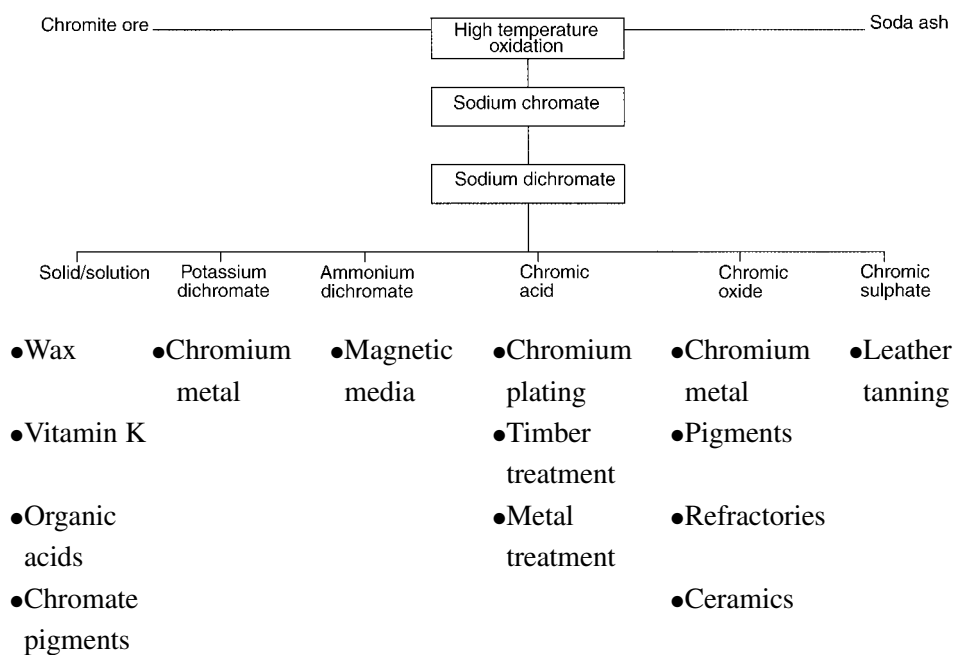

Figure 2. A typical flow sheet for chromium chemicals production.

3. Uses and toxicology of chromium chemicals

As the name chromium implies, the first applications were in the colour/pigment field but soon widened into leather tanning, chromium plating, timber preservation, corrosion protection, textiles, etching (Figure 2). Today, the use pattern is as shown below in Table III.

Around 90% of leather is tanned using chromium salts which convert a waste from the food industry into a valuable retail fashion commodity. Timber preservatives containing chromium, for example copper/chrome/arsenic (CCA), are the most effective currently available. Over 85% of the world demand for pure chromium

TABLE III

Chromium major markets

	Dichromate end use consumption (%)
Chromium sulphate	
Leather tanning	37
Chromic acid	
Metal finishing, timber preservation, audio tapes, catalysts	32
Chromic oxide	
Chrome metal for superalloys, pigments, refractories	21
Others	
Chromate pigments, oil drilling	10

metal is provided by the aluminothermit process using chromic oxide. Use of chromium oxide in industrial refractories is declining in applications where hexavalent chromium is generated during use and suitable alternatives are available.

The toxicological behaviour of chromium in both occupational and environmental situations is highly species-dependent; metallic chromium has no recognised toxicity; the relatively low acute toxicity of trivalent chromium is limited to salts of strong mineral acids; hexavalent chromium compounds display significant acute toxicity characteristics by all exposure routes and chronic toxicity particularly via inhalation and are classified/regulated accordingly.

Within Europe, for example, hazards associated with dangerous substances are communicated via standard risk (R) and safety (S) phrases and supported by hazard pictograms, for example as below for sodium chromate according to the 28th Adaptation to Progress to Directive 67/548/EEC:

R49: may cause cancer by inhalation.
R46: may cause heritable genetic damage.
R21: also harmful in contact with skin.
R25: and also toxic if swallowed.
R26: also very toxic by inhalation.
R37/38: irritating to respiratory system and skin.
R41: risk of serious damage to eyes.
R43: may cause sensitisation by skin contact.
R50/53: very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.

T+

N

4. Extraction process waste treatment and disposal

Despite many years of researching alternatives, landfill is still the world-wide industry standard today. Funded research continues because of the strategic importance of waste management to the industry. The more recent and larger western world factories are located close to existing or historic clay mining operations normally involved in refractory brick manufacture. Such plants generate approximately 1t of treated mineral waste per t of rated sodium chromate capacity employed, typically containing 8–12% Cr_2O_3. In modern no-lime plants the water-insoluble post-extraction residue is processed further to reduce the residual hexavalent chromium content to around 0.1–0.2% then passed to a chemical treatment stage prior to landfilling. Divalent iron- or sulphur-containing reducing agents are normally used and are capable of achieving residual hexavalent chromium levels < 1 ppm post-treatment.

High-lime process plants operating today collectively generate an estimated $600 \, kt \, y^{-1}$ of mineral waste as hazardous as the waste which is the main feature of historic landfill sites in other parts of the world. The challenge of successful treatment of high-lime process waste is considerably greater since it typically contains 30–40% calcium oxide equivalent together with significant ($>0.5\%$) levels of calcium chromate which dissolves slowly, influenced by solubility of the oxide. Also, the shape of the Eh/pH equilibrium curve (Figure 1) means that only very powerful reducing agents will be effective in reducing dissolved hexavalent chromium but still leaving the issue of residual toxicity due to lime content.

Over the 170+ years that the industry has existed, inability to landfill mineral waste has been the single most significant factor dictating factory closures, inevitably leaving some legacy behind in the form of toxic waste deposits often in

unknown locations. Perhaps the two most significant examples are in the Baltimore and Glasgow areas where commercial production first started and where it finally ceased in 1985 and 1967, respectively.

References

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