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Technology for the Combined Production of Chromium Metal and Ferrochromium

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Jinzhou Ferroalloy Works is part of an industrial complex producing ferroalloys, rare metals, and chemicals. The products include vanadium, titanium, chromium, manganese, molybdenum, zirconium, and hafnium. The chromium-series products are mainly chromium metal, chromic acid anhydride, sodium dichromate, ferrochromium alloy, and high-purity electrolytic chromium. In the process for the production of chromium metal and its compounds, a mixture of chromium ore, soda ash, and a large amount of calcareous additive is roasted with air in a rotary kiln, and then leached with water. The leach residue contains 0,3 to 0,5 per cent hexavalent chromium. This soluble hexavalent chromium is highly toxic. If the residue were not treated and removed, it would cause serious environmental pollution.

Because the Works produces chromium metal, chromic compounds, and ferrochromium simultaneously, the combined production technology for chromium metal and ferrochromium alloy has been studied since 1985. This process involves the oxidative roasting of chromium ore and soda ash in a rotary kiln without any calcareous additives, followed by leaching with water. The leach residue contains 38 to 42 per cent Cr_2O_3. After the residue has been dried and/or agglomerated, it is smelted in an electric furnace with coke and silica to form high-carbon ferrochromium. The present investigation was undertaken to eliminate hexavalent chromium pollutants in the leach residue, and to improve operating conditions during the roasting and leaching steps, as well as to improve the recovery.

This paper reviews the experimental work and the industrial-scale tests.

Introduction

The chromium-metal shop at Jinzhou Ferroalloy Works was set up in the early 1960's. In the early days of production, chromium metal was produced using the following production technology:

chromium ore → air and sodium-salt roasting → sodium chromate → sodium dichromate → chromium oxide → chromium metal.

The process was lengthy, and working conditions were adverse. Serious pollution by hexavalent chromium frequently caused production stoppages.

Research into the technology of chromium-metal production was started in 1969, and a new chromium hydrate route came into operation in 1972. The route is as follows:

chromium ore → air and sodium-salt roasting → sodium chromate solution → reduction with sulphur to chromium hydrate → chromium oxide → chromium metal.

This new technology has overcome the problems in the dissolution step that caused serious equipment corrosion and leaks during the course of sodium dichromate production. In addition, the process has been shortened, various residues containing hexavalent chromium have been eliminated, and poor working conditions have been improved.

A series of studies on methods for the treatment and use of the chromium leach residues have been conducted by Jinzhou and other local works. These tests had two main objectives.

Firstly, studies were undertaken to improve the production technologies and equipment. The aims were to decrease the amount of residue, to reduce the hexavalent chromium in the residue, and to reduce pollution. The tests[1] included the following:

(a) pelletization and roasting of a mixture of chromium ore with a small amount of calcareous additive
(b) roasting with a small amount of calcareous additive
(c) roasting without any calcareous additive
(d) roasting of a mixture of chromium ore and caustic soda without any calcareous additives
(e) low-alkali roasting without any calcareous additives.

The leach liquor was used for the production of chromium metal. The leach residue was used in the smelting of high-carbon ferrochromium in the so-called chromium metal–ferrochromium combined production process.

Secondly, studies were conducted on the reduction of the leach residue, reduction of toxicity, and comprehensive use of the residue. These studies[2-7] included the following:

(1) The residue containing hexavalent chromium was reduced with iron sulphite, alkali metal sulphite, sulphite, thiosulphate, etc. After the treatment, the residue was discarded and stockpiled.
(2) Residue containing hexavalent chromium was reduced and roasted with a carbonaceous reductant. The result-

ing residue was used for the production of construction aggregate (China Jinzhou Ferroalloy Works).

(3) Chromium leach residue was used for the production of calcium magnesium phosphate (China Hunan Ferroalloy Works), in brick manufacture (China Jinzhou Ferroalloy Works, Qingdao Red Star Chromate Works, and Changsha Chromate Works), as a glass colourant (China Qinhuangdao Glass Works), and as a flux for ironmaking or in iron-ore sintering (China Jinzhou Ferroalloy Works).

Some of the above-mentioned methods were used in production, but most methods were not adopted owing to economic or other constraints.

At present, the quantity of chromium leach residue stockpiled at the Works amounts to several hundred thousand tons since, for many years, only a small amount of chromium leach residues have been treated and used. An underground seepage-proof dam has been built around the residue stockpile, with a total catchment area of over 10 km^2. After many years of observation, it has been confirmed that the dam has achieved its objective and has prevented pollution. At present, the Works still accumulates chromium leach residue at a rate of over 10 kt/a.

Since the capacity of the dam is limited, it is necessary to seek effective measures for the treatment of chromium leach residues or for improved production technology to eliminate sources of pollution. A method is known for the production of ammonium chromium alum by the treatment of chromium ore with acid, following which chromium metal is produced from the ammonium chromium alum by an electrolytic process. This method was earlier adopted by some works. The small-scale tests and trial production of chromium metal and high-carbon ferrochromium on an industrial scale are reviewed in this paper.

Roasting of Chromium Ore without Calcareous Additive

It is known that the CaO content of chromium raw materials for the production of chromium chemicals is too high for the successful smelting of high-carbon ferrochromium. The high calcium content not only lowers the effective composition of chromium and iron in the ferrochromium but, more importantly, it causes the melting point of slag to exceed the permissible temperature range during smelting. In order to lower the melting point, a large amount of silica is required to be added. This increases the amount of slag, increases the consumption of electrical energy, and lowers the metal recovery. The investigation of chromium ore roasting without calcareous additions is therefore necessary for the combined production of chromium metal and high-carbon ferrochromium.

Roasting Procedure

Full-scale tests on calcium-free roasting were conducted in a rotary kiln of 2,3 m diameter by 3,2 m. Full-scale tests on the smelting of high-carbon ferrochromium using the leached residue from calcium-free roasting were conducted in closed electric-smelting furnaces with capacities of 3,5, 1,8, and 12,5 MVA. The flowsheet for the process is shown in Figure 1.

The main conditions during the full-scale tests on calcium-free roasting were as follows.

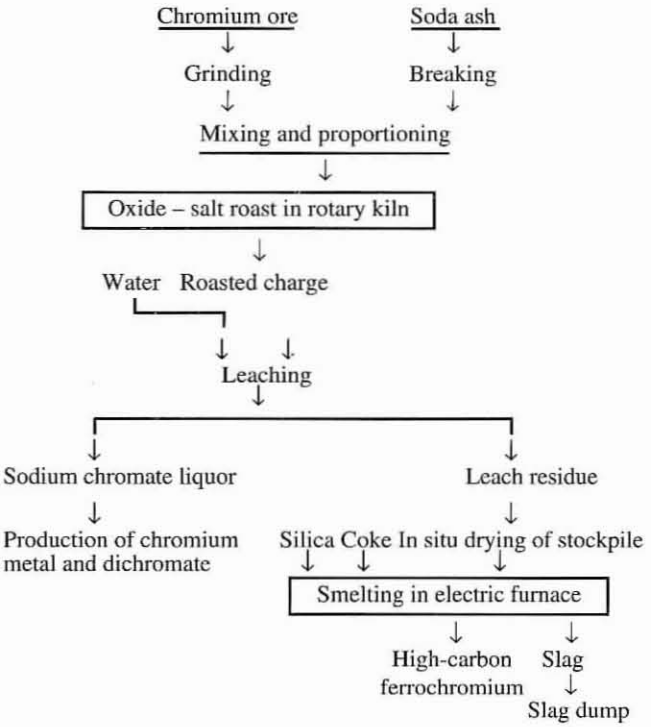

FIGURE 1. Flowsheet for the combined production of chromium metal and ferrochromium alloy

(1) Particle size of chromium ore: ≥85 per cent (by mass) – 180 mesh
(2) Amount of soda ash: 35 ± 5 per cent of theoretical requirement
(3) Temperature of roasting zone in the rotary kiln: 1000 to 1100 °C
(4) Temperature at the rotary-kiln feed end: 550 °C
(5) Pressure at the rotary-kiln feed end: 600 to 800 Pa
(6) Charge feed rate: 3 t/h
(7) Rotational speed of rotary kiln: 0,7 to 1,2 r/min
(8) Water temperature for leaching the roasted charge: ≥75 °C
(9) Countercurrent washing: 5 cycles
(10) Filter equipment: tank-type vacuum filter.

Results of Roasting Tests

The main results of the industrial-scale test on calcium-free roasting under conditions of low alkalinity are listed in Table I. The following conclusions were drawn.

(a) Calcium-free roasting can be utilized in industrial production under the same conditions as those used for chromium ore roasting with a calcareous additive and with the same equipment. All the production steps were successful, and the quality of the products was constant. The quality of the resulting sodium chromate liquor and the chromium oxide and chromium metal processed from the sodium chromate all exceeded that of the products of the calcium-containing roasting technology.

(b) The addition of soda ash was about 40 per cent of the theoretical amount. Problems were not experienced with accretions in the rotary kiln during roasting. The discharge consisted of spherical particles with good leaching and filtration properties. The leaching extraction was more than 97 per cent, an increase of 5 to 10 per cent over that obtained with calcium roasting.

TABLE I
THE MAIN RESULTS OF THE INDUSTRIAL-SCALE TEST ON CALCIUM-FREE, LOW-ALKALI ROASTING

Raw materials	Chromium ore	Cr_2O_3, %	SiO_2, %	ΣFe, %	MgO, %	Al_2O_3, %	CaO,%
		53,80	5,01	9,27	12,50	10,35	0,17
	Soda ash	Na_2CO_3, %	Chloride, %	Water insolubles, %		Roasting loss	
		>98	≤1,2	≤0,2		≤0,7	
Roasted charge		ΣCr$_2$ O, %	Water-soluble Cr_2O_3, %	Conversion of sodium chromate, %			
		43,83	12,08	27,56			
Leach liquor		Na_2CrO_4, g/l	SiO_2, g/l	Al_2O_3, g/l	NaOH, g/l	Na_2CO_3 g/l	Cl, g/l
		255,8	0,094	2,09	4,65	6,03	1,14
Leach residue		ΣCr_2O_3 %	Water–soluble Cr_2O_3, %		MgO, %	SiO_2, %	Al_2O_3 %
		43,83	0,24		13,94	5,11	9,84
		Fe_2O_3, %	CaO, %	ΣNa,%	Water–soluble Na, %	Acid–soluble Na, %	H_2O, %
		15,37	<0,5	3,60	0,70	2,70	20,8

TABLE II
COMPOSITION OF CHROMIUM ORES AND LEACH RESIDUES FROM THE CALCIUM-FREE ROASTING

Material	Cr_2O_3 %	SiO_2 %	ΣFe %	Al_2O_3 %	CaO %	MgO %	P %	H_2O %	ΣNa %
Indian ore	52,71	4,62	11,84	10,55	0,39	11,15	0,005	6,0	
Albanian ore	36,50	12,38	11,16	8,05	1,06	18,70	—	2,0	
Iranian ore	44,50	8,25	9,65	7,26	0,10	21,16	0,002	2,0	
China Xizang ore	52,55	5,24	9,27	10,16	10,17	16,72	—	1,0	
Chromium leach residue*	37,50	4,0	11,40	10,0	6,3	13,5	—	8 – 11	2,5

*Because chromium leach residue from calcium-free roasting was blended with that from calcium roasting, the Cr_2O_3 content in the leach residue decreased slightly, and the CaO content increased slightly

(c) The capacity of the rotary kiln increased substantially in comparison with calcium roasting. During the industrial-scale tests, the capacity of the rotary kiln increased by 27 per cent.
(d) The leach residue contained up to 43 per cent Cr_2O_3. The Cr/Fe ratio was more than 3. The residue accordingly met the needs of high-carbon ferrochromium production.
(e) Hexavalent chromium in the leach residue during calcium-free roasting decreased to less than 0,2 per cent, a decrease of 75 per cent compared with calcium roasting.
(f) The consumption of energy during calcium-free roasting was 35 per cent less than that during calcium roasting.
(g) The utilization of soda ash decreased notably. The unit consumption of soda ash per ton of sodium chromate increased by 15 to 20 per cent in comparison with that during calcium roasting.

Full-scale Smelting Tests

Full-scale tests on the smelting of high-carbon ferrochromium using leach residues high in chromium were conducted in electric furnaces with capacities of 3,6, 1,8, and 12,5 MVA. Because the chromium leach residue came from a stockpile, its moisture content was high (7 to 12 per cent). As it was difficult to charge only residue into the electric furnace, chromium ore and residue were charged in the correct proportions. The amount of residue was 20 to 50 per cent of the total charge. The chromium ores consisted of fine ore from India, lumpy ore from Albania, ore from Iran, and domestic lumpy ore from the Xizang Autonomous Region. The chemical analyses of the residues and chromium ores are listed in Table II.

When 40 per cent chromium leach residue was smelted in a 12,5 MVA electric furnace, the various economic and technological parameters exceeded those of the other two furnaces. The composition of high-carbon ferrochromium, the slag composition, and the main economic and technological parameters are listed in Tables III, IV, and V respectively.

Smelting Technology

The chemical composition of the chromium leach residues is similar to that of the fine chromite, except that the residues contain a small amount of chromate. Smelting by an electrothermic carbon-reduction process was therefore adopted. Owing to the presence of sodium in the residue, both the specific resistance of the charge and the viscosity of the slag decreased. During smelting, the melting point of the SiO_2–Al_2O_3–MgO slag is normally 1720 °C, and its viscosity is 0,7 to 1,2 Pa·s but, when the slag contains 1,0 to 2,5 per cent sodium oxide, its viscosity decreases[8] by 20 per cent to about 0,85 Pa·s. Because of this viscosity decrease,

TABLE III
COMPOSITION OF THE HIGH-CARBON FERROCHROMIUM PRODUCED USING THE CHROMIUM LEACH RESIDUE FROM CALCIUM-FREE ROASTING IN A 12,5 MVA CLOSED ELECTRIC FURNACE (AVERAGE OF 58 SAMPLES)

Cr %	Si %	C %	P %	S %	Fe %
63,79	2,88	8,12	0,031	0,019	Balance

TABLE IV
COMPOSITION OF THE SLAG OBTAINED USING THE CHROMIUM LEACH RESIDUE FROM CALCIUM-FREE ROASTING IN A 12, 5 MVA CLOSED ELECTRIC FURNACE

Cr_2O_3 %	SiO_2 %	CaO %	MgO %	Al_2O_3 %	ΣNa %
3,17	32,9	2,36	38,03	18,35	0,77

TABLE V
MAIN ECONOMIC AND TECHNOLOGICAL PARAMETERS OF THE COMBINED PROCESS AND THE CHROMIUM HYDRATE PROCESS IN A 12,5 MVA CLOSED ELECTRIC FURNACE

Unit consumption	Combined process	Chromium hydrate process
Chromium ore, t/t	1,088	1,714
Electrical energy, kWh/t	3 394	3 229
Coke, t/t	0,434	0,454
Chromium–containing leach residue, t/t	0,541	
Recovery of metal, %	89,70	88,96
Percentage of pass	100	98,99
Capacity, t/d	65,319	65,057

the Al_2O_3 content of the chromite in the charge is less important, and the improved fluidity of the slag can improve the separation of metal from slag and increase the recovery of chromium.

Crucial Operating Parameters

The chromium leach residue has a fine particle size and a high moisture content, and therefore smelting can generate a large amount of smoke and dust, and cause fluctuations in the pressure in the electric furnace. The leach residue and chromium ore were used in correct proportions to maintain a relatively stable pressure in the furnace, and to avoid the collapse of a large amount of the charge in the furnace, which would result in deterioration of the furnace operation. The leach residue was 20 to 30 per cent of the total charge in the open electric furnace, and 40 per cent in the closed electric furnace. During smelting, the voltage of the furnace was increased slightly, and the current correspondingly decreased. The secondary voltage of 148 V was increased to 156 V. The electrode was moved once 30 minutes before tapping; the electrode cannot be moved 10 minutes before tapping, because the charge would collapse. Because of the small content of CaO in the leach residue, the amount of silica was increased during charge proportioning. The alkalinity of the slag, $(MgO+CaO)/SiO_2$, was controlled in the range 1,1 to 1,2, and its melting point was below 1720 °C. This can prevent the tumbling of slag in the furnace, collapse of the charge, rising of the electrode, and tapping difficulties, etc.

Problems and Discussion

The full-scale tests on the combined production of chromium metal and ferrochromium were conducted successfully. The combined process can completely eliminate the hexavalent chromium from the leach residue in the production of chromium metal, and thus avoid environmental pollution. The economics of the process are reasonable.

The main problems in the process are the high unit consumption of soda ash, and the smoke and dust pollution.

The results of the full-scale tests show that calcium-free roasting has the following advantages compared with calcium roasting: capacity is increased, energy consumption is decreased, and metal recovery is increased substantially. However, the unit consumption of soda ash is increased. In order to explain this increase, a mass balance for sodium was analysed. The results of the analysis are listed in Table VI.

TABLE VI
MASS BALANCE FOR SODIUM IN CALCIUM-FREE ROASTING

Input	Output			
Soda ash	Leach liquor	Leach residue	Volatilization loss	Adsorption of kiln lining
100%	85%	14%	1,0%	Zero

Sodium in the feed liquor exists mainly in the form of sodium chromate, sodium aluminate, sodium silicate, and free alkali. It is difficult to determine the form in which sodium exists in the feed leach residue. This component of sodium is the main reason for the high consumption of soda ash. For this reason, an analysis of the physical phase composition of the roasted charge after calcium-free roasting was conducted. The results are listed in Table VII.

Table VII shows that some of the water-soluble sodium in the leach residue, such as sodium chromate, sodium aluminate, and sodium silicate, was not leached. The water-insoluble sodium compounds were mainly sodium aluminium silicate and 6 $NaAlSiO_4 \cdot Na_2CrO_4$. The latter compound was formed readily during calcination. During calcium roasting, aluminium and silicon in the charge are fixed by calcium to form $Ca(AlO_2)_2$ and $CaSiO_3$. During calcium-free roasting, aluminium and silicon react with sodium, and therefore it is certain that the consumption of soda ash during calcium-free roasting will be higher than that during calcium roasting. The 6 $NaAlSiO_4 \cdot Na_2CrO_4$ that forms not only increases the sodium consumption, but also consumes some of the chromium as Na_2CrO_4. The utilization of alkali and recovery of chromium are thus reduced. At present, it is difficult to accurately control the phases that form during calcium-free roasting, and it is therefore very difficult to achieve the same unit consumption of soda ash as in calcium roasting.

Pretreatment of Chromium Leach Residues

Owing to the high moisture content and fine particle size of the leach residues, a large amount of smoke and dust is generated during smelting. Drying of the leach residues makes the smelting technology more economic and more reasonable.

The residue is blended with a given mass of powdered coke, and is granulated (briquetted) before storage. The agglomerate is heated and prereduced simultaneously in a rotary kiln. The hot charge of prereduced briquettes is fed to an electric furnace. This process can improve the opera-

TABLE VII

PHYSICAL PHASE COMPOSITION OF THE ROASTED CHARGE FROM THE CALCIUM-FREE ROASTING OF CHROMIUM ORE

Composition	Molecular formula	Melting point, °C	Rel. density	Magnetic property	Water solubility	Acid solubility	Content in roasted charge, %
Sodium chromate	Na_2CrO_4	792	2,72	NM	Soluble	Soluble in dilute acid	20 – 56
Sodium vanadate	$NaVO_3$	630		NM	Soluble	Soluble in dilute acid	0,01 – 0,05
Free soda	Na_2CO_3	351	2,53	NM	Soluble	Soluble in dilute acid	0 – 20
Sodium silicate	Na_2SiO_3	1 088	2,4	NM	Soluble	Soluble in dilute acid	0,02 – 1,0
Sodium aluminate	$NaAlO_2$	1 800		NM	Soluble	Soluble in dilute acid	0,15 – 5,0
Magnesia	MgO	2 800	3,58	NM	Insoluble	Soluble in dilute acid	0 – high
Chromite	$(Fe{\cdot}Mg)Cr_2O_4$		4,6 – 4,9	Weak	Insoluble	Insoluble in hot conc. acid	Low – high
Sodium aluminium silicate	$NaAlSiO_4$	1 526	262	NM	Insoluble	Soluble in dilute acid	0 – med
Sodium magnesium silicate	$Na_4\ MgAl_4SiO_3O_{12}$	>1 200		NM	Insoluble	Soluble in dilute acid	0 – high
	$6\ NaAlSiO_4 \cdot CrO_4$			NM	Insoluble	Soluble in dilute acid	0 – 10
Red iron ore	α–Fe_2O_3	1 565	5,24	Mid	Insoluble	Soluble in strong acid	0 – low
Magnesioferrite	$Mg(Fe{\cdot}Al)_2O_4$	1 750	4,4 – 4,6	Strong	Insoluble	Soluble in hot conc. acid	0 – high
Non-morphologic	Contains Na, Mg, Al, Si, Fe					Soluble in dilute acid	Low – high

NM – Nonmagnetic

tional conditions and economics of smelting, and create more favourable conditions for the industrial-scale operation of the combined process. At the same time, the design of the electric furnaces should be improved so that they meet the needs of the smelting operation for a lower specific resistance of the charge.

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