Comprehensive Treatment Technology of Chromium Leached Residues

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Abstract

The paper introduces a new kind of treating chromium leached residues (CrR) technique. With the CrR as flux addition, a self-flux sinter is made with removal centage of chromic acid ions in the CrR more than 99%, then to produce Cr-bearing pig iron by a blast furnace melting with the sinter. The main features of the technique are: (1) making use of the CrR in large amounts; (2) complete detoxification and no secondary pollution; (3) recovery chromium resources with obvious environmental and social and economic benefit; (4) with a broad applicability.

Background

The Origin and Harm of Chromium Leached Residues

A chromium leached residue (referred to simply as "CrR" from now on) is the waste product that resulting from leaching the clinker with water, which is obtained from a high temperature roasting of chromate with Na_2CO_3 and dolomite etc. during chromium metal production. 9~11kg CrRs are removed off with producing 1kg chromium metal .Generally, it is abandoned or dumped as industrial rubbish.

Being the CrR with 0.8~1.2% water or acid solubility chromate (chromate or chromic acid ion-CrO_4^{2-}), in general, this severely toxic substance is seriously harmful to human health and ecology environment. A investigation indicated that the workers engaging in chromium metal production for a long time frequently arose in diseases of respiratory system and dermatosis like schneiderian membrance erosion, septal perforation, chrome sore and rash etc. Furthermore, higher cancer morbidity (mostly in lung-cancer), due to contact infection or aspirating chromate-bearing dust. Studies have shown that chrome oxidizing calcine is substantial carcinogen. If a large amount of CrR is dumped freely without any detoxification treatment and safeguard measure, it would result in such rather serious environmental pollution as surface water pollution. Especially, cause fish death, a drop for yield of agricultural product and various human diseases occurrence in emergency situations. Many chromium or chromate manufactures in the world were forced to stop or convert production or closedown due to no effective protection measure for chrome pollution. Therefore, treatment for the CrR has been concerned about much greatly from early time.

Technical Reviews for Treatment of the CrR

Over the past 30 years, experts at home and abroad have undertaken a considerable amount of research work to deal with the CrR pollution problems, and made many fruits, some of which have been put into commercial applications,

China began to study this problem in 1960, Many treatment methods have been tried.

For treatment ways of the CrR, the general trends in other countries tend to first detoxicate the CrR then store or bury it. Only a few head for developping comprehensive utilization of the CrR, without remarkable commercial benefits yet.

Treatment methods of the CrR can be classified several types as follows:

1. To dump the CrR in a yard with anti-leakage function, covering plates on it in case of wind and rain.
2. To close the CrR. For example, cement sealing.
3. Reduction detoxification. First reducing Cr^{6+}in the CrR then storing or bury it. There are 2 methods; i.e. dry reduction detoxification (DRD), wet reduction detoxification (WRD).
4. The CrR comprehensive utilization (CrRCU).

The CrR is made good use during producing various correlative products or manufactured articles with some profits. Moreover, chromate in the CrR is reduced in the processing.

So far it has been universally realized that the best solution of treatment ways of the CrR is to make self-flux sinter with the CrR as a raw material then produce allowed pig iron.

Study on Making Self-fluxing Sinters with the CrR and Melting Chromium Alloyed Pig Iron

Fundamentals

Table 1 gives CrR chemical compositions, it suggests that the CrR may be used as agent of fusion in sintering production.

For ferrous materials, it is considered that iron concentrate, ferrous powder by magnetic separation, mill roll scale, dust of a revolving furnace, and vanadium tailings, which is the leaching residue from V_2O_5 production (iron content about 40 wt%, here under referred to as VT), etc. By using the CrR, ferrous materials and coke breeze, in a high temperature sintering, a self-flux sinter that meets a blast furnace-slag requirements is made.

The difficulty for the sinter production is that chromate in the CrR has to be reduced completely in sintering processing.
Reduction mechanisms of chromate in sintering processing are: being in the presence of carbon, iron metal and ferrous oxide in a blend, in high temperature sintering processing, the order of chromic acid ion being reduced is from Cr to Fe. It is obtained from △F-T Relationship on reducing oxides of Cr and Fe that CrO_3, CrO_2 are reduced first, following iron (Fe), with a part of Fe_2O_3 having been reduced to FeO, CrO_3, CrO2 are further reduced, Free energy changes of above reactions are all large negative values, so chromic acid ions have many opportunities to be reduced, and the equilibrium constants are numerous.
For instance,

$$4/3CrO_3+2C=2/3Cr_2O_3+2CO$$
at 1500K, $K=5.128\times10^{25}$

Therefore, in high temperature atmosphere, chromate being reduced by many reducing reaction..The CrR can be thoroughly changed into stable Cr^{3+} valance state in the sinter which industrial test and sintering production practice have proved.

The Treatment Process

The process flow diagram is shown in Fig.1.

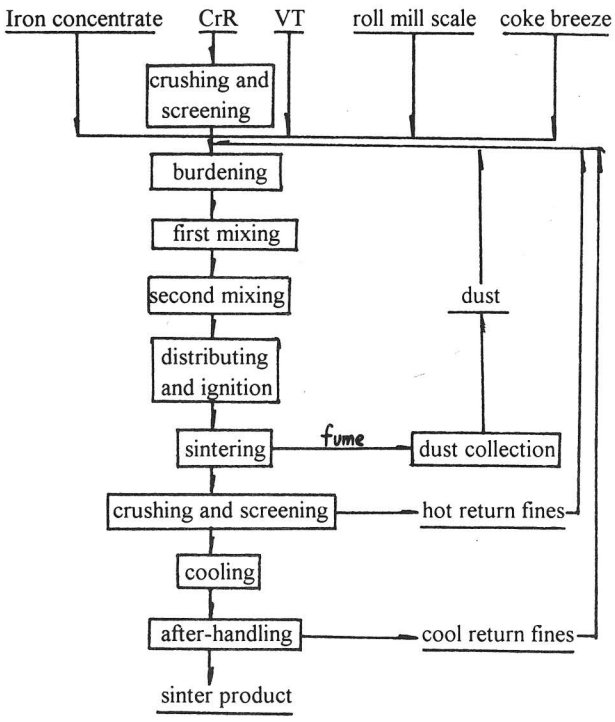

Figure 1. The sintering process flow diagram

The CrR being crushed and passed through screening to obtain the desired size fractions, was mixed with iron concentrate, mill roll scale and coke breeze, as well as the VT from V_2O_5 processing. Through first mixing, second mixing, igniting, sintering, crushing and screening etc., sequential procedures, a quality sinter product is made.

Chemical compositions of the main raw materials are shown in Table 1,2. By selection a $18M^2$ sintering machine, in industrial-scale trial 30 thousand tons CrRs are utilized with annual 120 thousand tons sinter products, such products are all used for iron making.

Table 1. Chemical Compositions of CrR, VT, Iron Concentrate, Roll Mill Scale Used in the Process, wt%

	CrR	VT	Iron concentrate	Roll mill scale
Fe	6.82	32.50	66.25	69.39
CaO	25.46	1.12	0.45	0.11
MgO	22.41	2.26	0.73	
SiO_2	5.96	17.04	6.80	3.52
Cr_2O_3	5.92	4.48		
V_2O_5	trace	1.02		
S	0.085	0.065	0.047	
P	0.018	0.023	0.023	0.026
CrO_4^{2-}	2.32	0.004		
FeO	3.59	2.73	16.68	46.80
H_2O	8.50	8.50	6.70	3.24

Table 2. Chemical Constituent of Coke Used in the Process, wt%

Fixed carbon	74.15	
Ash matter	22.29	S: 0.607; SiO_2: 61.90; Al_2O_3: 26.39
Volatile component	3.56	

The Trial Results

The aim of the investigation reported here was first to produce a qualified sinter product to meet requirements for a blast furnace, then melt out chromium alloyed pig iron by the use of the sinter with reasonable technical and economic indexes.
It was studied that the sintering process, for example, effect of Carbon addition rate, the CrR addition rate and sinter basicity on removal centage of CrO_4^{2-}, and ironmaking with the sinter by a blast furnace.

- Basicity in the Table is $R=(CaO+MgO)/SiO_2$

Table 4 indicate that slightly high Carbon addition rate is favorable for removal efficiency of CrO_4^{2-}, the CrO_4^{2-} content in the sinter is lower as the sinter basicity is higher.

Table 4. Chemical Analyses of the Alloyed Pig Iron

No	C	Mn	S	P	Si	Cr	V	Ti
1	3.80	0.70	0.05	0.06	0.80	1.70	0.28	0.20
2	3.78	0.66	0.041	0.08	1.68	2.05	0.31	0.50

2. The experimental result for ironmaking with the sinter by blast furnace.

The ironmaking trial was carried out with a $18.6m^3$ blast furnace.
The chemical composition of the product is shown in Table 4.
The elements recovery is shown in Table 5.

1. Carbon addition rate, CrR addition rate for the blend and sinter basicity experiments. The result is shown in Table3.

Table 3, Chemical Compositions of the Sinter

No.	Carbon addition rate wt%	Basicity	Analysis of the sinter, wt%											
			TFe	FeO_2	CaO	SiO_2	MgO	Al_2O_3	P_2O_5	S	V_2O_5	TiO_2	Cr_2O_3	CrO
1	2.53	1.26	49.5	12.0						0.013			1.94	5.80
2	3.1	1.26	47.5	13.8	6.68	9.36	5.13	3.03	0.037	0.014	0.38	1.68	3.38	4.24
3	3.7	1.26	50.1	17.2						0.022			2.44	2.90
4	4.1	1.26	47.3	20.6						0.031			2.87	3.57
5	4.5	1.26	47.4	21.5						0.033			3	2.23
6	3.5	1.23	50.8	16.8	6.25	9.43		2.06	0.037	0.024	0.31	1.14	1.8	62.44
7	3.5	1.58	47.9	14.0	7.82	8.84	5.43	2.00	0.037	0.015	0.22	0.77	1.71	49.06
8	3.5	1.78	48.7	22.4	8.14	8.31	6.16	1.96	0.037	0.029	0.19	0.40	2.55	26.76
9	3.5	1.9	48.4	16.9	8.35	7.87	6.59	1.93	0.037	0.017	0.15	0.31	2.0	19.40
10	3.5	2.36	51.4	18.7	8.69	6.52	6.71	1.87	0.037	0.019	0.14	0.31	1.78	28.99
11	3.5	1.79	48.3	18.9	7.69	7.78	6.22	1.97	0.037	0.020	0.21	0.65	3.07	44.6

Table 5. Recovery for the Elements, wt%

No.	V	Cr	Fe	Ti
1	76.0	89.0	97.2	4.1
2	75.0	82.0	97.3	3.8

Discussion

CrO_4^{2-} Reduction

It is observed that there are 2 significant factors affecting CrO_4^{2-} removal efficiency, i.e. carbon addition level, sinter basicity. As above stated, carbon is a main reductant of chromate, so carbon addition level affects directly reduction degree of CrO_4^{2-}, at meantime, determines temperature in sintering processing too. In as far as reducing CrO_4^{2-}, higher carbon addition level and sintering temperature are beneficial to reduction reactions. It appears, however, that a large amount of Fe_2O_3 will be reduced to FeO with an excess of carbon above 1500k, causing FeO increase in sinter and , thereby lowering reducibility of sinter. In order to solve the problem, it is necessary to find out a adequate carbon addition level and control a proper sintering temperature range. The range of carbon addition level in the study is from 4.32 to 4.98 wt%.

Effect of carbon addition rate on Cr^{2-} content is given in Figure 2.

2. The sinter basicity has a influence on CrO_4^{2-} content is given in Figure
3. The sinter basicity has a influence on CrO_4^{2-} removal. It appears that from Figure 3 CrO_4^{2-} in sinter is decreasing with increasing the sinter basicity.

Sinter mineralogy has shown that the amount of magnochromite increases considerably in sinter, as well as chromium content in maguctite, with increasing carbon addition rate; as the same is ,with increasing sinter basicity. Therefore, to increase carbon addition rate and sinter basicity have favor influences on chromate removal.

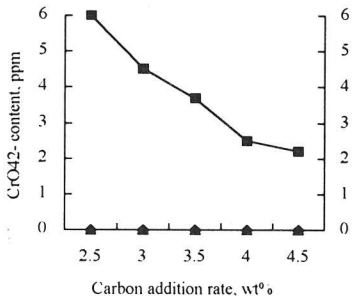

Fig.2. Effect of carbon addition rate on CrO_4^{2-} content in the sinter

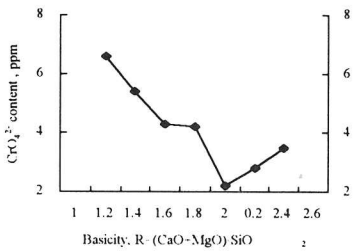

Fig.3. Effect of basicity on $CrO4^{2-}$ content in the sinter

Sinter Metallurgical Performance

Metallurgical performances of the sinter made from the CrR, may affect directly technic and economic indexes of a blast furnace iron making. Hence, it would be desirable to obtain superior reducibility sinter with a high strength and low RDI level. The trials proved that increasing carbon addition rate favors sinter strength and CrO_4^{2-} removal, but has an advers
an adverse effect on desulfurization, and reducibility of sinter,

On the Ironmaking Technology

The self-flux sinter product made from the CrR and the VT is different from an ordinary sinter. Therefore, to make blast furnace run smoothly and melt flow fluently, to obtain optimum technic and economic indexes and quality alloyed pig iron with Cr, V, Ti, etc., it is necessary to consider influences of many complex factors and adopt special technology in the process of ironmaking. In a blast furnace smelting processing, above 1520k, the order of metal elements reduced by C is Cr, Mn, Nb V, B, Si, Ti, etc. along with Cr, the easiest reduced one except Fe; but Ti, the hardest one.

Hence, to make sure full recovery of Cr and V, and raise Cr and V content in the pig iron, it is favorable to increase temperature in a blast furnace hearth.

The VT addition causes increasing the amount of TiO_2 in the sinter, as well as oxides of alkalinous metal such as Na_2O and K_2O, obviously. This property has a influence not to be ignored on smelting processing. In high temperature reduction atmosphere, on the one hand. TiO_2 in molten-slag is reduced to low valence oxides Ti_3O_5, Ti_2O_3,TiO, etc. After carbonization, the oxides can form TiC, TiN, and its continuous sosoloid Ti (C.N), which form dispersed suspension condensing the slag, thicking wall of a furnace, raising a furnace bottom, even leading heat coagulation to affect the normal operation. On the other hand larger amount of oxides of alkalinous metal Na_2O, K_2O may dilute the slag, and scour furnace bottom and hearth lining. As above two aspects interaction in a system, with proper operating conditions, the slag viscosity for a blast furnace normal smelting can be obtainable.

Conclusions

It is a method that producing self-fluxing sinters using the CrR as a raw material and smelting Cr-bearing pig iron. Its major characteristics are as follows:

1. CrO_4^{2-} in the CrR is reduced or detoxicated completely. The CrO_4^{2-} content remaining in sinter product is no more than 5ppm. Further by a blast furnace smelting, chromium enters pig iron phase as alloyed element
2. The process is suitable to large-scale commercial application with using a great deal of the CrR. To take selecting a $18M^2$ sinter machine for example, the CrR will be treated up to 30 thousand tons per year with no secondary pollution.
3. The treatment of the CrR by adopting the technology not only eliminate the CrR pollution but also effectively recover chromium and other valuable elements, providing with the CrR comprehensive utilization (CrRCU).
4. For ferrous raw materials, in addition to iron concentrate, local waste materials can be used such as vanadium tailings (VT), ferrous dust, roll mill scale, etc. to produce self-fluxing sinters and smelt chromium-bearing pig irons.

References

1. Wei S. K., Thermodynamics of Metallurgy Processing (Shanghai, SH: Shanghai Science and Technology Press, 1980), 12.
2. Deng S. Q. et al., Technology on a Blast Furnace Iron Making (Beijing, BJ: Metallurgical Industry Press, 1980), 294~302.
3. Goteliburg A. D., ed., A Blast Furnace Smelting Processing (Beijing, BJ: China Industry Press, 1956), 289~292.
4. Dong Y. C. et al., Knowledge of a Blast Furnace Smelting (Beijing, BJ: Metallurgical Industry Press, 1991), 86~87.
5. Zhang H. T. et al., "Making Self-fluxing Sinters with the V. T. and CrR-Comprehensive Utilization of the V. T. and CrR and Study on Hexvalant Chromium Removal (one) ,Ferroalloy", (1987), 7~13
6. Zhang H. T. et al., "Smelting Vanadium-bearing Pig Iron with the V. T. and CrR Sinter by Simulation a Blast Furnace-Comprehensive Utilization of the V. T. and CrR and Study on Hexvalant Chromium Removal (two) ,Ferroalloys", (1987), 26~30
7. Zhang G. J. et al., "Study on High Bacisity and High MgO Sinter", Sintering and Palletizing, 2(1992), 17~22
8. Li W. H., "Test on Addition of Magniferous lime in Sintering," Sintering and Palletizing, 2(1992), 23~26