A novel method for innocent treatment of reducing dephosphorization slags

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ABSTRACT

A novel method for treating the Reducing Dephosphorization(RDP) slags environmentally was developed by the present authors, with manganese fine ore being applied as oxidizer. The minimum amount of manganese fine ore used to oxidize calcium phosphide (Ca_3P_2) into calcium phosphate ($Ca_3(PO_4)_2$)completely has been calculated out firstly, and it should be over 1.388 times of the RDP slags, to assure the products after treatment could be reused as the materials for FeMn production in the ferroalloy industry. Then experiments for disposing RDP slags were carried out in an induction furnace and the products were detected by XRD, XRF analysis and the discoloration of $AgNO_3$ test paper respectively. The XRD results showed that the Ca_3P_2 in the reducing slags are oxidized, and there is $Ca_3(PO_4)_2$ in the product after treatment, which is innocuous. The stability of the disposed slags has been detected as well after treatment 2 days and 30 days and the results showed that the RDP slag disposed by sufficient manganese fine ore is lumpy and has no P escape after exposed in the air for 30 days, which indicated the feasibility and stability of current method.

Keywords: Reducing Dephosphorization (RDP), Manganese fine ore, Calcium phosphide (Ca_3P_2), Phosphine gas (PH_3), Calcium phosphate ($Ca_3(PO_4)_2$)

INTRODUCTION

The conventional Argon Oxygen Decarburization (AOD) process and Vacuum Oxygen Decarburization (VOD) process for 300 series stainless steel production have limitation of Silicon (Si) content in Ferronickel (FeNi) alloy, viz. Si is not exceed 1.0 wt%, which can be named as low-silicon FeNi here. However, the most common processes for FeNi production in China are Sintering - Submerged Arc Furnace (SAF) and Rotary Kiln - Electric Furnace (RKEF) smelting process with nickel laterite ores as materials, during which, it needs to add carbon or other reductants with the aim to meet the requirements. In this case, high silica in laterite ores will be reduced into the melt. And it is proved by the practical experience as well that it is difficult to produce low silicon FeNi with nickel laterite ores containing high silica, hence it will be cost effective to produce a FeNi alloy with high silicon content (more than 10%) and utilize its characteristics in the production. This ferroalloy can be named as high-Si FeNi. Based on this background, Chu et al.[1, 2] has invented an electric-silicothermic method for 300 series stainless steel production, which takes high-Si FeNi as the source of silicon in silicothermic process. Chromium concentrates were charged and reduced by this high-Si FeNi so as to produce un-refined stainless steel, with the process flowchart shown in Figure 1. The un-refined stainless steel metal is then provided to the stainless steel plants or followed by AOD/VOD process to produce stainless steel directly.

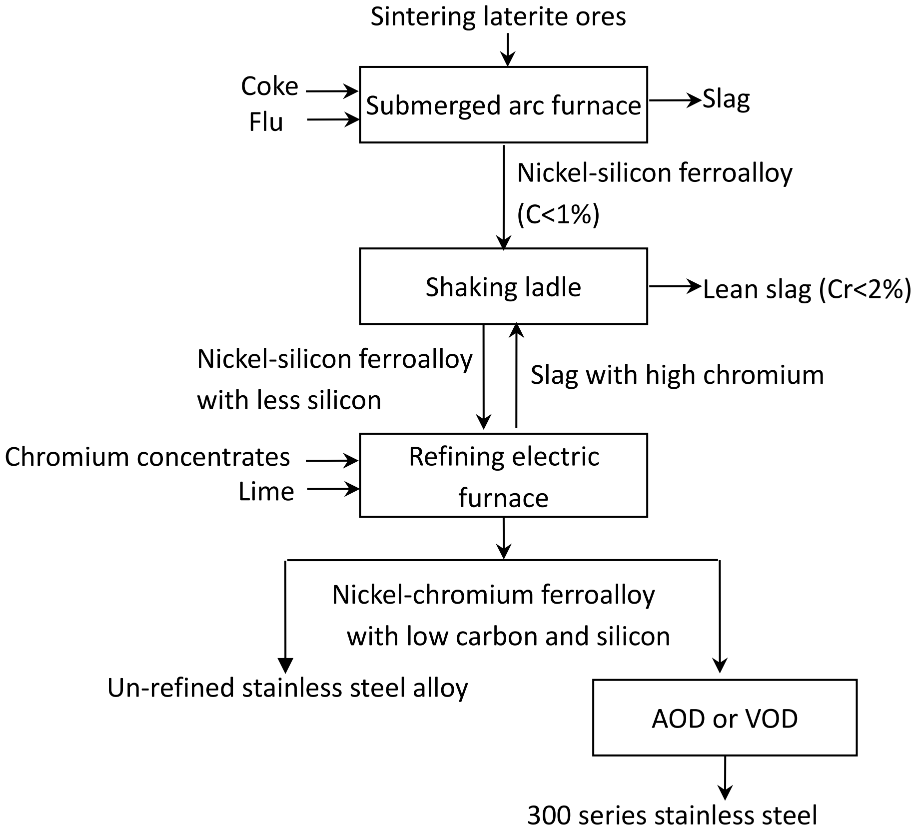

Figure 1. 300 series stainless steelmaking process with electric-silicothermic method.

One needs to point out that the phosphorus (P) in this high-Si FeNi alloy is necessarily controlled to meet the requirements for stainless steel production. P content in FeNi alloy is strictly limited when FeNi is used as the base material for the production of stainless steel since it is known that P in steel will increase the segregation, and have a bad effect on the mechanical properties of steel such as corrosion resistance and welding performance. Generally, there are two methods for dephosphorization of ferroalloys, oxidizing dephosphorization and reducing dephosphorization. For dephosphorization of current high-Si FeNi alloy, reducing dephosphorization (RDP) process is in preference to oxidizing method because of its protection of silicon and valuable metals as well as its excellent dephosphorization effect.

However, the slags obtained from RDP process contain calcium phosphide (Ca_3P_2). Ca_3P_2 can generate hazardous phosphine gas (PH_3) when it is exposed in the moist atmosphere at room temperature, as shown in equation $Ca_3P_2(s)+6H_2O(g)=3Ca(OH)_2(s)+2PH_3(g)$. PH_3 is detrimental to environment as well as human being[3]. A small amount of inhalation will lead to dizziness, headaches, sickness and vomiting. Severe PH_3 poisoning damages to lungs, heart, liver and kidney, and even cause death. Hence, it is essential to dispose the RDP slags environmentally. The proper way to manage RDP slags innocuously not only relates to the success of the electric-silicothermic method for 300 series stainless steel production, but also provides good solutions for processes which generate RDP slags.

There are few studies reported the valid method for RDP slag treatment. Katayama et al.[4] proposed a process to deal with RDP slags with injecting oxygen to vapourize phosphorus before separating slag from steel, however, the rephosphorization of steel occurred when the reaction duration increasing. Oh et al.[5] invented a method to stabilize RDP slags with spraying high pressure air and inert gas into it, which utilized the oxidizability of oxygen in air. Shin and Park [6] also injected oxygen on the molten RDP slags to convert Ca_3P_2 into innocuous $Ca_3(PO_4)_2$ successfully, which proves injecting oxidizing gas is effective for disposing RDP slags innocuously. But the resultants obtained from injecting oxidizing gases can not be recycled. Guo et al. [7] reported that there is a way to dispose RDP slags with the waste nitric acid, however, there will be H_2S and NH_3 generated although no PH_3 come out. There are several other methods [7-9], which are almost conceptual and have little applicable prospect, furthermore the resultant after treatment can just be discarded without any use. The present researchers are trying to develop a novel method to handle the RDP slags innocuously, meanwhile, the products could be reused. Oxidizing substances which are suitable for converting Ca_3P_2 into innocuous $Ca_3(PO_4)_2$ is the consideration for disposing the RDP slags environmentally. For this point of view, combined with the background of ferroalloy production, manganese fine ore is applied to process the RDP slags to realize the aim mentioned above.

THEORETICAL ANALYSIS

Thermodynamics analysis

Thermodynamic calculation was firstly carried out to investigate the feasibility of manganese ore oxidizing RDP slags. The main composition of manganese fine ore is manganese oxide. The standard Gibbs free energy changes for the reactions between different manganese oxides(MnO_2, Mn_2O_3, Mn_3O_4, MnO)and Ca_3P_2 to form $Ca_3(PO_4)_2$ were calculated and plotted in Figure 2. It is seen from Figure 2 that the standard Gibbs free energy of various manganese oxides reacting with Ca_3P_2 are all negative at the temperature of 1000-1800℃, which indicates that manganese ore can react with Ca_3P_2 in RDP slags produced in the metallurgical processes, such as FeNi production or chromium containing steel production .

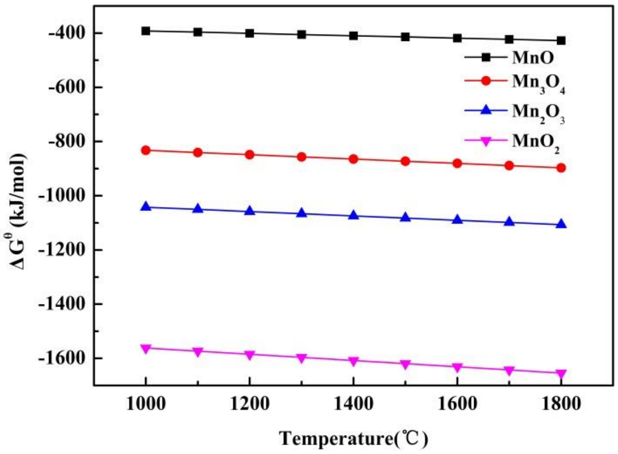

Figure 2 ΔG^0 change of Ca_3P_2 reacting with different manganese oxides(MnO_2 ,Mn_2O_3 ,Mn_3O_4 ,MnO) at temperature of 1000-1800℃

It is seen from Figure 2 that the reaction sequence of Ca_3P_2 with manganese oxide is MnO_2 >Mn_2O_3 >Mn_3O_4 >MnO. But manganese oxides with high valence are unstable at high temperature. MnO_2 will be decomposed to Mn_2O_3 when temperature is above 753K, Mn_2O_3 is decomposed to Mn_3O_4 when temperature is above 1203K while Mn_3O_4 is decomposed to MnO when temperature is above 1450K. MnO is not easy to decompose and considered to be stable under the general conditions. In order to estimate the proper amount of manganese fine ore for innocuous treatment of RDP slags, Mn in the ore is assumed as MnO completely in the current study. In this case, the following reaction is considered as the main reaction for disposing RDP slags through manganese fine ore.

$$Ca_3P_2(s)+8MnO(s)=Ca_3(PO_4)_2(s)+8Mn(s) \quad (1)$$

Theoretical Calculation

It is demonstrated that manganese fine ore can convert Ca_3P_2 in the RDP slags into innocuous $Ca_3(PO_4)_2$ under steel and ferroalloy making temperature by thermodynamic analysis. The present novel method attempted to dispose the hazardous Ca_3P_2, meanwhile the products can be reused as raw materials for FeMn alloy production. It is essential to calculate out the theoretical minimum amount of manganese ores used for innocent treatment of RDP slags in this way, because the quality of manganese ore is limited in the FeMn alloy production process. The requirements of the manganese fine ore used for FeMn alloy production are high manganese content, less gangue content, less harmful impurity, high strength and appropriate lumpiness. The specific composition requirement of the manganese ore used for FeMn alloy production is shown in Table 1. In order to reuse the manganese ore after treating RDP slags, parameters of Mn content, Mn/Fe and P/Mn need to be considered for design.

Table 1 The content requirements for manganese ore used in ferroalloy industry

Critical content of Mn (wt%)	Average content of Mn (wt%)	Mn/Fe	P / Mn	SiO_2 (wt%)
>25	>30	>2-4	≤0.006	<35

Since there is no data reported for compositions of RDP slags generated from high-Si FeNi production currently, the present authors estimated the content of it firstly. Assumed the initial P content of high-Si FeNi alloy is 0.05 wt% and the final P content in melt needs to be 0.02 wt% after RDP treatment to fit the requirements of stainless steel making by the silicothermic method[10]. The slag used as dephosphorization agent is $CaO-CaF_2$(6:4), and the mass of it is 10% of the alloy. The main RDP reactions are

$$2CaO(s)+[Si]=SiO_2(s)+2[Ca] \quad (2)$$

$$3[Ca]+2[P]=Ca_3P_2(s) \quad (3)$$

Assume that 10% of [Ca] that decomposed from CaO will react with P in the melt to form Ca_3P_2. The calculated compositions of dephosphorization slag after RDP process is shown in Table 2 and the P content in the RDP slag is 0.3089 wt%.

Table 2 The calculated compositions of RDP slags

Item	**CaO**	**CaF_2**	**Ca_3P_2**	**SiO_2**
Wt%	53.42	41.19	0.91	4.48

In the present study, the manganese fine ores used for disposing the RDP slag is shown in Table 3.

Table 3 The content of manganese fine ore

	Composition/wt%							Size distribution/%	
	Mn	Al_2O_3	Fe	SiO_2	CaO	P	MgO	-6.7mm	6.7-75mm
	49.59	4.48	0.69	8.53	0.99	0.075	0.45	2.7	97.1

Based on equation (1), it is calculated out that the theoretical weight of manganese fine ore completely reacting with Ca_3P_2 in 1000g RDP slag is 28.30g. However, if the products after treatment could meet the critical requirements of Mn($Mn \geq 25\%$) and P/Mn ratio ($P/Mn \leq 0.006$) of manganese ores used in FeMn alloy production, the minimum weight of manganese fine ores adopted in the innocent treatment process will be 672.18g and 1388.07g obtained from the calculation respectively. Therefore, the ratio between manganese fine ores and RDP slags should be over 1.388, to assure the products after disposing RDP slags could be reused as the materials for FeMn production in the ferroalloy industry.

EXPERIMENTS

Experimental device and materials

Experiments were conducted in a 10 kg induction furnace. Magnesium oxide materials were adopted for crucible lining. High-Si FeNi, ferrophosphorus, lime, calcium fluoride and manganese fine ores were applied as the experimental raw materials. In order to get better dephosphorization effect, P in melt was set higher than the real production.

Since reducting dephosphorization rate is influenced by various factors, and the related fundamental research is limited, a pre-experiment was carried out to analyze the P content in the dephosphorization slag after RDP process, with the purpose to determine the method of application of manganese fine ore. The pre-experimental results showed that the P content is 5.85 wt% in the RDP slag. Following the calculation steps illustrated in Theoretical Calculation part, the exact weight of manganese fine ores reacting with RDP slags was estimated as 552.51g. The experiments were conducted by varying in the weight of manganese fine ores, insufficient amount, appropriate amount and excessive amount, with the aim to study the influence of manganese fine ore on the effect of treatment. The experimental scheme is shown in Table 4.

Table 4 Experimental scheme

No.	**High Si FeNi**	**Fe-P**	**Lime**	CaF_2	**Manganese fine ore**
1#	3.04kg	0.2kg	0.4kg	0.26kg	0.3kg
2#	3.04kg	0.2kg	0.4kg	0.26kg	0.6kg
3#	3.04kg	0.2kg	0.4kg	0.26kg	1.2kg

Experimental procedures

High-Si FeNi and Fe-P was firstly added into MgO crucible, then dephosphorization slag($CaO:CaF_2=6:4$，20% of metal mass) was charged into the crucible after the alloy melted completely and reacted for 1 minute. Sampled the slags fast by a metal bar, packaged it in a tinfoil and sealed it into a stock bottle very quickly in order to prevent the RDP slag expose to the moist of the air. Charged the manganese fine ores rapidly, reacted for 15 minutes, sampled, tapped and took samples again.

RESULTS AND DISCUSSIONS

Treatment effect tested by discoloration detection with $AgNO_3$ test paper

Discoloration detection with silver nitrate ($AgNO_3$) test paper was firstly adopted to detect the existence of Ca_3P_2 in slag in the present experiments. The color of the $AgNO_3$ test paper is varied depending on the concentration of PH_3 in the air, from light gray to silver black. The discoloring sensitivity of $AgNO_3$ test paper is 0.03mg/m^3. China state standard for PH_3 concentration in air is less than 0.3 mg/m^3. Hence, the RDP slag is considered as innocuous if the color of $AgNO_3$ test paper has no change during testing.

In current test, both RDP slags and disposed slags were examined by $AgNO_3$ test paper. The samples was put into a conical flask, then several drops of water were dripped into the slag with a rubble dropper and the operator observed the color variation of $AgNO_3$ test paper. The schematic diagram for the test is illustrated in Figure 3. It was found during the experiments that all the $AgNO_3$ test paper used for testing RDP slags turned black which indicated PH_3 generation from RDP slags. While, for disposed slags, papers examined 2# and 3# disposed slag remained invariant color which indicated there is no Ca_3P_2 in the disposed slags. But 1# disposed slag changed the paper into black, showed appearance of PH_3, which is mainly because the manganese fine ore used in 1# experiment is inadequate and there is remained Ca_3P_2 in the disposed slag.

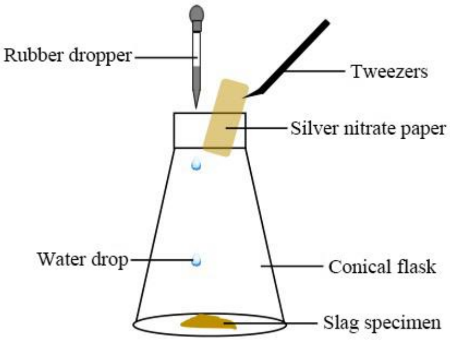

Figure 3 The schematic diagram of discoloration detection with $AgNO_3$ test paper

Treatment effect examined by XRD analysis

Up to now, there is hardly any report on the major components of RDP slag as well as the disposed slag. In the current study, both RDP slags and the disposed slags were detected by XRD in order to further analyze the composition of slag. The XRD patterns are shown in Figure 4. Figure 4(a1), (b1) and (c1) presented the XRD patterns of RDP slags obtained from test 1#, 2# and 3# respectively and the results shown the main phases in the RDP slags are CaF_2, Ca_3P_2 and Ca_2SiO_4, which validated the existence of Ca_3P_2 in the RDP slags. It is also seen MgO appears in the RDP slag obtained in 3# experiment, which is because the experimental crucible is not changed during this three experiments, as the consequence, corrosion of crucible and dissolution of MgO into slag takes place.

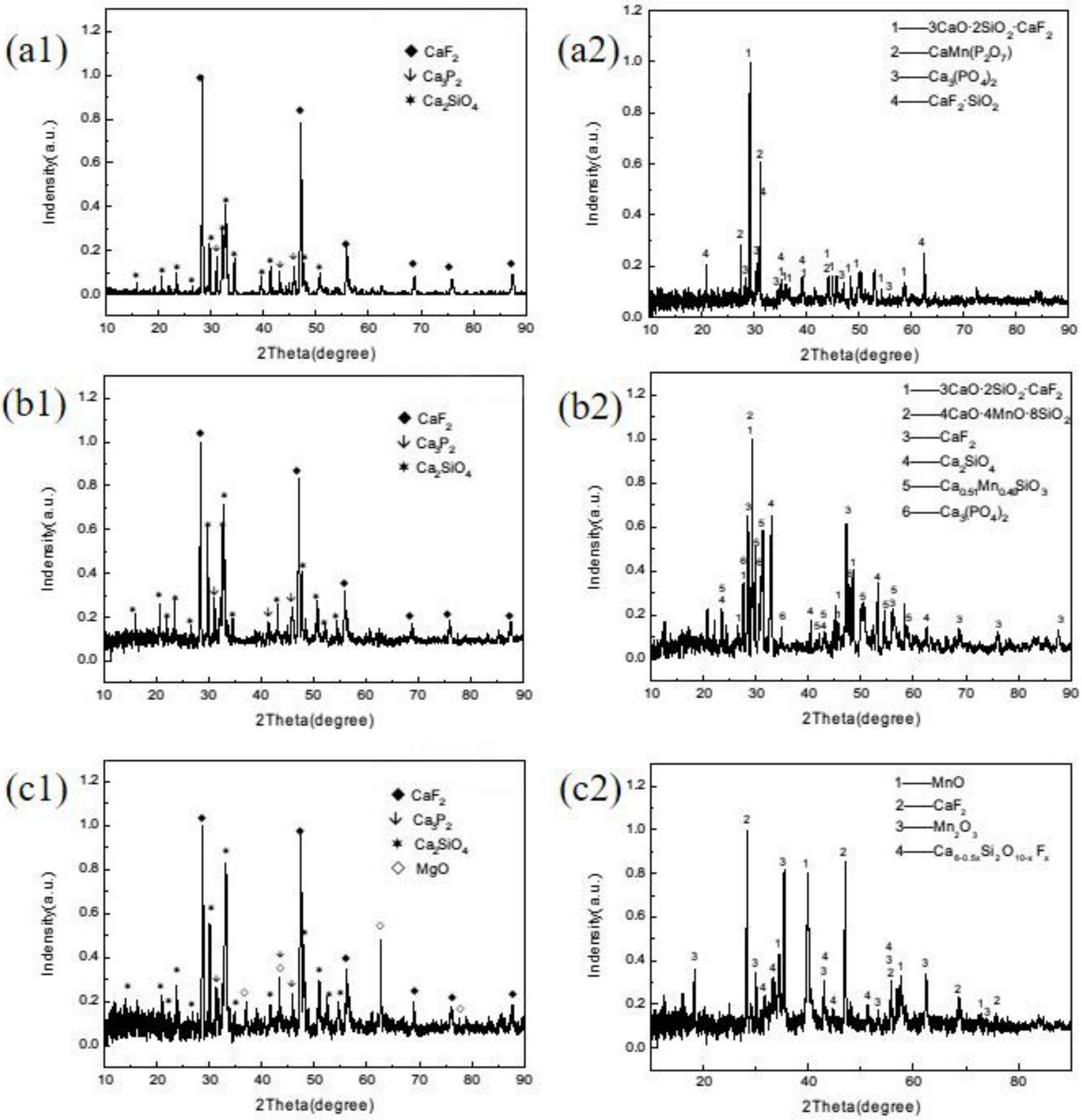

Figure4 The XRD patterns of RDP slags and disposed slags (a1:1# RDP slag, a2:1# disposed slag, b1:2# RDP slag, b2:2# disposed slag, c1:3# RDP slag, c2:3# disposed slag)

After the treatment by manganese fine ores, the phosphorus in 2# and 3# RDP slags has been oxidized into higher valence states to form $Ca_3(PO_4)_2$, which is innocuous, as shown in Figure 4(a2) and (b2). There are MnO, Mn_2O_3, CaF_2 and complicated compound containing O, F, Ca and Si in 3# disposed slag, whereas, it is not found $Ca_3(PO_4)_2$ in it. That is maybe because very large amount manganese ores (twice of the required amount) used in 3# experiment leads to the low content of compound containing P which is hard to detect by XRD. But 3# disposed slag had no PH_3 generation during the test of $AgNO_3$ test paper, which indicated 3# RDP slag is also innocent.

The stability of current treatment method

In order to confirm the feasibility of the current method and the stability of the product, the slags obtained from 3 different group experiments (in total 6 samples including RDP slags and disposed slags) were exposed in the air for 2 days and 30 days respectively. Then the slags were sent for XRF analysis, and the surface morphologies were observed and recorded as well. The phosphorus content in the slags variation with the storage time is shown in Figure 5. It is seen that there are significant declines of phosphorus content of 1#, 2# and 3# RDP slags from 2 days to 30 days, mainly because Ca_3P_2 reacted with H_2O in the air and the phosphorus escaped as the PH_3 formation. A similar trend was observed for 1# disposed slag from 2 days to 30 days on account for lack of manganese fine ore in 1# experiment.

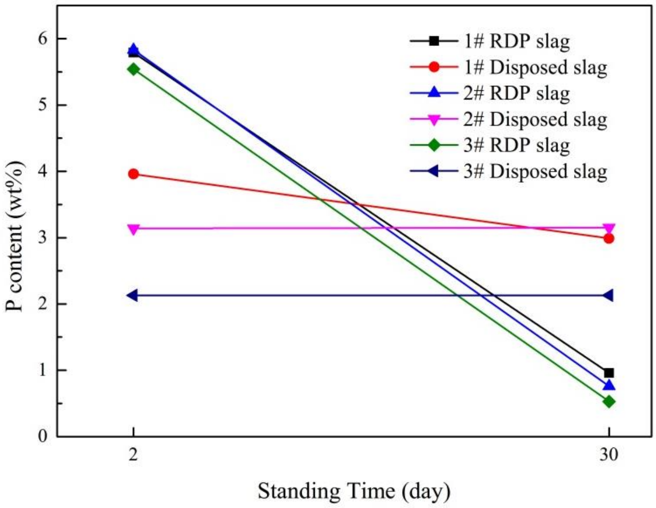

Figure 5 Phosphorus content of slag variation after 2 and 30 days exposed in the air

However, as seen from Figure 5 that, the phosphorus content in 2# and 3# disposed slags, which are treated by sufficient manganese ore has nearly no variation after 30 days, showed as P content being a horizontal line from 2 days to 30 days, which indicated that the Ca_3P_2 has been oxidized completely by manganese fine ores into the stable components. In this case, there will be no PH_3 generation during storage, hence it can be concluded that manganese fine ore can be applied in innocent treatment of the RDP slags effectively.

Besides, the macroscopic feature of the slags was observed to further understand the treatment effect. The 1# disposed slag pulverized after exposing in the air for 5 minutes and produced stinking smell, which would be the smell of PH_3. However, for 2# and 3# disposed slags, the experimental resultants are lumpy and they keep the shape well after 30 days treatment as well, as shown in Figure 6, which indicated the stability of the disposed slags and the good effect of current method. This lumpy product can be used as reactant to produce ferromanganese when the RDP slag mixes with a large number of manganese ore to meet the requirements of raw materials. In this case, the product for innocent treatment of RDP is recycled and somehow, the sintering process for fine manganese ores will not be necessary. Hence, this novel method not only utilizes the sensible heat of the slag effectively, but also recycles the RDP slag environmentally and cost effectively.

It is also found that with the increase of the amount of manganese fine ore, the compactness of disposed slag raises. But one needs to notice that, appropriate size and quantity of cavity in the disposed slags can catalyze the reaction from manganese ore to Mn on account of kinetics, hence it is meaningful to study the optimized amount of manganese ore for treatment in the practice, which will be investigated in future.

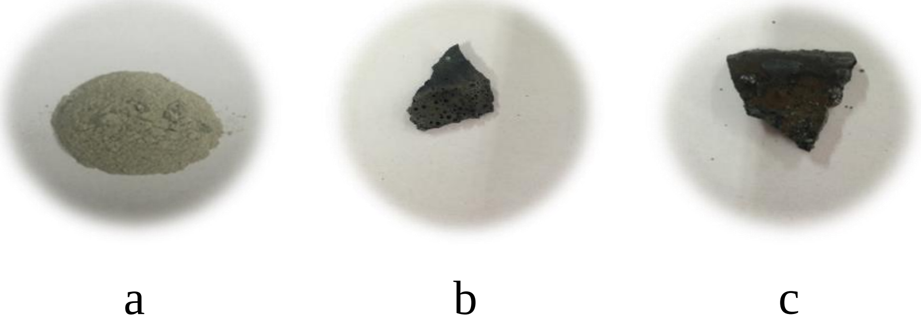

Figure 6 Surface morphologies of disposed slag after 30 days exposed in the air (a:1# disposed slag, b:2# disposed slag, c:3# disposed slag)

CONCLUSIONS

A novel method for innocent treatment of RDP slags is proposed. Thermodynamic calculation and induction furnace experiment verified the feasibility of this method. Following items could be concluded by current study.

(1) Under the given circumstances, the minimum quantity of manganese fine ore used to oxidize Ca_3P_2 into $Ca_3(PO_4)_2$ completely is 1.388 multiple of RDP slag to insure the product could be reused in the FeMn production.

(2) Through XRD analysis of RDP slags and disposed slags, it was confirmed that the main dephosphorization product is Ca_3P_2. Sufficient amount of manganese fine ore can effectively oxidize the phosphorus of reduction state to high valence states, further treat the RDP slag innocuously.

(3) After 30 days placement of disposed slags which were treated by sufficient manganese fine ore, the phosphorus content in the resultant is stable, and the surface morphologies remained lumpy, which indicated the feasibility and stability of current method.

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