

Cite this article as: Huo Yingda, Li Fubao, Zhu Xiaoping, et al. Effect of Glass Slag Properties on Palladium Recovery from Waste Pd/Al₂O₃ Catalyst via Smelting-Collection Process[J]. Rare Metal Materials and Engineering, 2022, 51(10): 3646-3654.

ARTICLE

Effect of Glass Slag Properties on Palladium Recovery from Waste Pd/Al₂O₃ Catalyst via Smelting-Collection Process

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Abstract: The isothermal phase diagram of SiO₂-CaO-Al₂O₃ slag system was calculated by FactSage6.4. By fixing the agent MgO content at 8wt% and controlling Al₂O₃ content lower than 35wt%, a reasonable liquidus temperature and mineralogical phase of the glass slag were obtained. The effects of temperature, binary basicity $w_{\text{CaO}}/w_{\text{SiO}_2}$ and Al₂O₃ content on viscosity of the feasible SiO₂-CaO-Al₂O₃-MgO slag were investigated by the rotating spindle method and simulating calculation. Results show that with increasing the temperature, the slag viscosity decreases, Al₂O₃ content increases from 15wt% to 35wt% and binary basicity $w_{\text{CaO}}/w_{\text{SiO}_2}$ increases from 0.3 to 1.0 according to the univariate investigation. It is known from the smelting experiment using iron as collector that the recovery rate of palladium increases with increasing the mass fraction of waste catalyst in material system, and it increases first and then decreases with continuously increasing the basicity and temperature. With the waste Pd/Al₂O₃ catalyst used in this study and using the optimized slag ingredients of about 30wt% Al₂O₃, 8wt% MgO and binary basicity $w_{\text{CaO}}/w_{\text{SiO}_2}=0.5$, the recovery rate of palladium reaches 99% and the residual palladium in glass tailing is less than 4.50 g/t.

Key words: waste catalyst; secondary resources; glass slag; palladium recovery; pyrometallurgy

The catalytic activity of platinum group metals (PGMs) revolutionizes the chemical processes, which is contributed to their widest application in preparation of catalyst^[1-5]. Palladium is one of the most consumed PGMs and its global demand is rising, which will exceed 300 t by 2025. However, more than 70% of palladium consumption is focused on catalyst manufacturing^[6,7]. Undoubtedly, the produced waste palladium catalyst will continue to increase. Correspondingly, the natural abundance of palladium is very limited and the extraction process from raw ore is extremely complicated^[8-10]. So, it makes sense to use the waste catalyst as significant secondary resources of palladium to alleviate the shortage. What's more, since the hazardous materials, such as soluble/leachable organic and inorganic compounds exist, the waste catalysts are harmful to the environment and listed as hazardous waste^[11,12]. It is particularly critical to put forward an efficient and harmless recovery technology.

Recovery of PGMs from solid wastes such as electronic waste, anode slime, and waste catalysts involves various

metallurgical and chemical methods. Hydrometallurgical method is an achievable and widely acceptable technology in the past years, which have been conducted for the recovery of PGMs from solid waste by leaching PGMs with hydrochloric acid and oxidants system or cyanide solutions^[13-17]. However, several inevitable and evident shortcomings are exposed from practical application^[10,18-20]. For instance, toxic and decomposed agents such as NaCN in leaching solution can generate NO_x, posing a threat to the environment. Other problems such as considerable waste residues and liquids, the over-consumption of reagents and volatile recovery rate of PGMs should also not be neglected^[10,18-20]. Biological methods have the advantages of low cost, simple equipment, and less pollution, and also have the disadvantage of long processing time and low productivity^[21].

Pyrometallurgical process is the primary and effective approach to recover PGMs from solid waste, especially widely used in treatment of waste catalyst for its unique advantages such as simple operation and flow process, and

Received date: February 09, 2022

Foundation item: National Key Technology R&D Program (2019YFC1907504); Liaoning Educational Committee General Program (LJKZ0166)

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enormous potential for large-scale industrial production. Many famous enterprises such as Umicore, Badische Anilinund-Soda-Fabrik, and Johnson Matthey around the world have extensively applied pyrometallurgical process to recovery PGMs^[22,23]. In particular, the smelting collection process plays the most significant role in pyrometallurgical recovery of PGMs from waste catalysts^[23]. Researchers have paid extensive attention to the theory of base metal collection and presented many reports about different collectors such as lead^[1,24], copper, matte^[23,25,26], iron and its oxides^[27-29], and waste printed circuit boards^[30,31]. Nevertheless, lead, copper, nickel, as well as their oxides usually cause health and environmental risks due to their chemical properties of heavy metal. In addition, copper and nickel matte collections have a complex refining process, which needs large scale investment. Conversely, iron is not only a low-cost and readily available collector with a strong affinity for PGMs, but it also can be refined by conventional hydrometallurgical process. Therefore, iron collector has been widely used in previous investigations, and its reliability has been proved. The plasma arc furnace process uses a mixture of crushed waste automotive catalyst, iron collector, reducing agent of carbon and fluxes as material system, smelted at 1773~2273 K, and then enriched with PGMs in the molten metallic iron alloy. By this process, the recovery of Pt, Pd, and Rh is up to 98%, 98%, and 97%, respectively^[23,29]. However, when the smelting temperature is higher than 1873 K, the silicon dioxide can be reduced to monatomic silicon and further form the Si-Fe alloy which is extremely difficult to dissolve in the subsequent hydrometallurgical refining, resulting in a changeable recovery rate. Therefore, it is necessary to control the smelting temperature. Based on the above urgent need, a novel and pragmatic method namely mineral phase reconstruction process was proposed^[1]. The key to this process is to find a slag system with low melting point according to the composition characteristics of catalyst.

Generally, physicochemical properties of melted slag are important impact factors on metallurgical process^[32-35]. However, the specific research on melted slag properties to recover PGMs from waste catalyst by smelting-collection process is very limited. In this study, a novel and reasonable glass slag was proposed for achieving efficient treatment of waste Pd/Al₂O₃ catalyst. For one thing, the glass slag with reasonable properties can not only achieve energy saving and consumption reducing, but also benefit to maintain a stable and high recovery rate of palladium. For another, the glass slag from smelting process has no threat to the environment due to the strong anti-rain erosion performance and other weathering resistance. Ultimately, the hazardous waste catalysts can be processed into environment friendly and harmless glass slag^[36-39], and reused as raw material for manufacturing kinds of glass and other functional materials^[40-42].

In this work, a typical and practical SiO₂-CaO-Al₂O₃-MgO glass slag system was proposed, specifically for the recovery of palladium from waste Pd/Al₂O₃ catalyst by smelting-

collection process, and the viscosity of the feasible SiO₂-CaO-Al₂O₃-MgO slag was investigated using both the rotating spindle method and simulating calculation. Then, the optimum technology parameters were obtained by the practical smelting experiment using iron as collector. The alloy product and glass slag in this study were tested by XRD, XRF, SEM and ICP (inductively coupled plasma) method. This work provides a novel and significant foundation for efficient recovery of palladium from waste Pd/Al₂O₃ catalyst.

1 Experiment

1.1 Experiment materials

The waste catalyst in cylindrical particles used in this study was obtained from catalytic hydrogenation reaction in chemical industry, and supplied by a catalyst recovery company in Jiangsu province, China. Before use, the harmful volatile and moisture were completely removed by high-temperature roasting process. The main chemical composition of the waste Pd/Al₂O₃ catalyst was tested by EDTA, XRF and ICP. The mass percent of alumina and silica was 99.22wt% and 0.42wt%, respectively, and the content of palladium was 1595.3 g/t. So, the melting point of the waste catalyst will be very close to 2327 K, which is difficult for conventional smelting process. Slagging is an effective solution to achieve the conventional smelting process and the slag system of SiO₂-CaO-Al₂O₃-MgO was chosen due to its applicable properties. The waste catalyst was crushed into powder to increase its specific surface area which is beneficial to the mixture and smelting processes subsequently. The fluxes such as SiO₂, CaO and MgO, Al₂O₃ and metallic iron collector powder were analytically pure and dried at the temperature of 423 K for 24 h before use to make sure the complete removal of moisture. In order to meet the high temperature and reduce the impact of impurities, high-purity graphite material was used for preparation of smelting vessel.

1.2 Experiment process

Firstly, the isothermal phase diagram of SiO₂-CaO-Al₂O₃ basic slag system was calculated by FactSage6.4 for selecting a reasonable composition. Then, the fluxes, Al₂O₃, iron collector and waste catalyst were accurately weighed according to the experiment scheme. These above weighed material in groups were fully mixed and sealed for subsequent experiments. The viscosity of slag with various compositions (MgO 8wt%, Al₂O₃ 15wt%~35wt% and binary basicity w_{CaO}/w_{SiO_2} 0.3~1.0) and temperature (1673~1973 K) were measured by the rotating spindle method and calculated by FactSage6.4. Lastly, the smelting experiment was carried out by resistance furnace with molybdenum disilicide heating unit. The effects of binary basicity and smelting temperature on recovery rate of palladium were evaluated. The mass of waste catalyst involved in each static smelting experiment was 200 g, and the mass ratio of iron collector to waste catalyst was 0.2, i.e. 40 g, and after these materials were fully mixed with fluxes, they were held in the furnace with argon atmosphere for 1 h. After the smelting process, the crucible was removed from the

furnace and the melted material was allowed to completely solidify by air-cooling. Later, the hot and solid products were removed for further water quenching process, and then the ferroalloy was separated from slag, cleaned, and weighed for subsequent assays. The specific diagram of flow sheet in this work is shown in Fig.1.

The content of palladium in glass slag and ferroalloy in smelting process were analyzed by ICP method, and the recovery rate of palladium was defined as:

$$R_{pd} = A_p / (A_p + S_p) \times 100\% \quad (1)$$

where R_{pd} is the recovery rate of palladium, A_p is the mass (g) of palladium concentrated into the ferroalloy phase, S_p is the mass (g) of palladium remained in the glass slag phase.

X-ray diffraction (XRD, PANalytical X'pert PRO diffractometer, $2\theta=5^\circ\sim90^\circ$, Cu K α radiation) of the cooled glass slag and ferroalloy powders was conducted to detect the characteristic of phase. The detailed compositions of waste catalyst and glass slag were measured with X-ray fluorescence (XRF, ZSX Primus II, Rigaku Corporation, Japan). The SEM (SEM-EDS, SU800) was employed to obtain microscopic images and EDS patterns of the alloy.

2 Results and Discussion

2.1 Properties of the SiO₂-CaO-Al₂O₃-MgO slag system

The system of SiO₂-CaO-Al₂O₃-MgO is selected as target slag due to its wide use in pyrometallurgy and glass manufacturing fields^[43,44], which is beneficial to the subsequent resource utilization. Fig. 2 shows the liquidus isotherms diagram of SiO₂-CaO-Al₂O₃ ternary system calculated by FactSage 6.4. It can be seen that when the temperature is about 1773 K, the alumina content of slag is 15wt%~35wt%, and the optional content of SiO₂ and CaO is 35wt%~70wt% and 10wt%~50wt% in the liquid region, respectively; CaAl₂Si₂O₈ and Ca₂Al₂SiO₇ are the main phase included in the slag system.

MgO acts as basic oxide and oxygen supplier which breaks

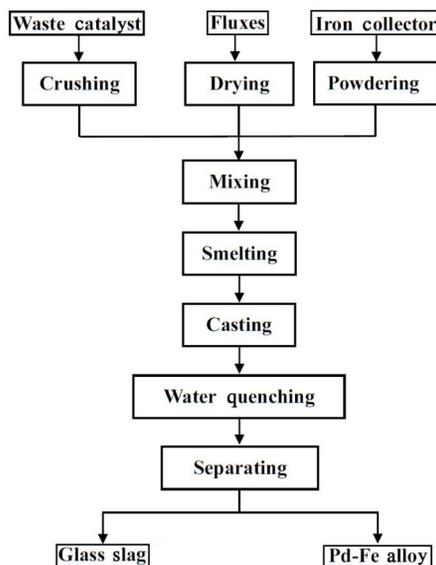


Fig.1 Flow sheet of the developed process

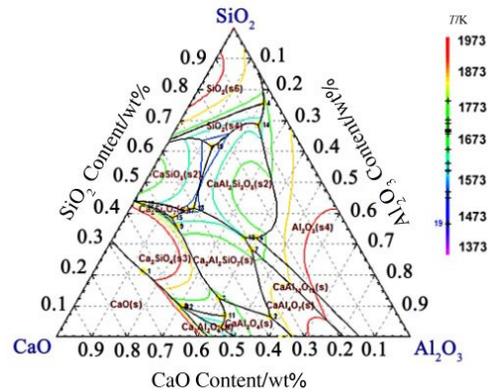


Fig.2 Liquidus isotherms diagram of SiO₂-CaO-Al₂O₃ ternary system

the discrete silica network and renders the slag more fluid. So, liquidus temperature of the slag system decreases with increasing MgO content in a certain range^[44]. This is consistent with the result of theoretical calculation shown in Fig. 3: the liquid region expands evidently with increasing MgO from 1wt% to 8wt%. Therefore, it is a good solution to add an appropriate amount of MgO to further reduce the melting point of slag, which ensures that the smelting process is lower than 1873 K^[29-31]. In the present study, the content of MgO in SiO₂-CaO-Al₂O₃-MgO slag system is fixed at about 8wt% to meet the requirement of the low melting point of slag with high Al₂O₃ content from 15wt% to 35wt%.

The viscosity and liquidus temperature of slag system are important factors in the smelting process, which are usually determined by the composition or basicity^[32,40,44]. The change of basicity will inevitably change the properties of the quaternary slag system and affect the metallurgical behavior. Fig.4 shows the measured and calculated viscosity of the slag system with different binary basicity $C/S(w_{CaO}/w_{SiO_2})$ and Al₂O₃ content. It is observed that the viscosity decreases subsequently with C/S increasing from 0.3 to 1.0 and Al₂O₃ content increasing from 15wt% to 35wt%. This might be attributed to the modification effect of CaO and Al₂O₃ on the network structure of molten slag according to the previous Ref. [45-47]. It is believed that SiO⁴ units and Si tetrahedral ions are contained in the network structure of silicate slag. Si tetrahedral ions are bonded through bridging oxygen. The non-bridging oxygen and free oxygen are produced through destroying the Si-O bonds of the Si tetrahedral ions in SiO₂ when the basic oxides such as CaO are added to the slag system. Generally, in the matter of mobility, the bridging oxygen is lower than non-bridging oxygen, so the depolymerized silicate leads to reduced slag viscosity. Therefore, it is beneficial to decrease the viscosity of molten slag by increasing the C/S .

2.2 Effect of binary basicity w_{CaO}/w_{SiO_2} on palladium recovery

Based on the above results, the effect of binary basicity C/S on recovery rate of palladium was evaluated by smelting

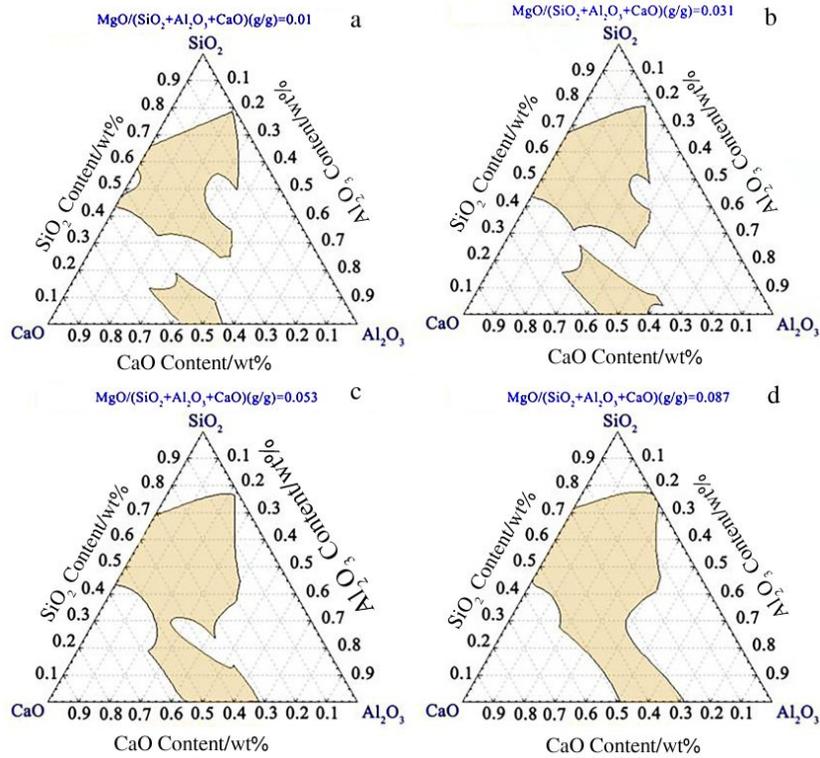


Fig.3 Change of liquid region with MgO content in SiO₂-Al₂O₃-CaO-MgO ternary system under 1500 °C/1.01×10⁵ Pa

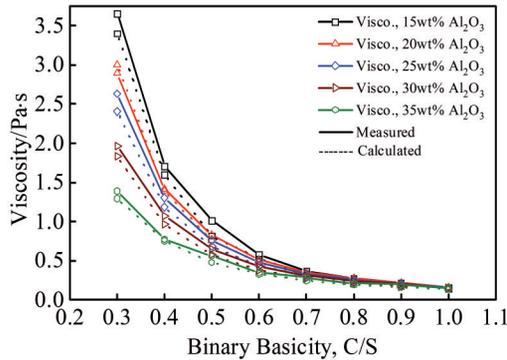


Fig.4 Viscosity of quaternary slag system with different binary basicity C/S and Al₂O₃ content at 1823 K

experiment at 1823 K, and the corresponding results are shown in Table 1. It can be seen that the palladium recovery rate initially exhibits a significant increase with the increase of the C/S and then reaches a maximum at a C/S of 0.5~0.6. Subsequently, palladium recovery rate decreases with further increasing the C/S. This might be attributed to the variation of viscosity with increasing C/S which is a significant factor on the change of recovery rate of palladium. Usually, the separation speed of metallic phase from molten slag is dominated by viscosity, i.e. a low viscosity of molten slag can improve the collision frequency between metals and facilitate the sedimentation of the metallic aggregate. The separation velocity can be estimated by Eq.(2) which is formed by Stokes law according to the previous work^[28,48].

Table 1 Palladium recovery at different compositions of glass slag with the smelting temperature of 1823 K (%)

Binary basicity, C/S	Waste catalyst/wt%				
	15	20	25	30	35
0.3	65.42	73.66	81.56	85.14	87.38
0.4	76.36	85.35	91.74	94.95	98.35
0.5	83.73	94.51	98.15	99.17	98.94
0.6	88.12	94.82	96.11	97.93	97.81
0.7	85.64	91.39	93.83	95.61	95.88
0.8	83.57	88.12	90.90	92.68	93.14
0.9	82.09	85.51	88.76	91.27	91.53

$$v_T = (\rho_m - \rho_s) d_m g / (18\mu) \tag{2}$$

where v_T is the terminal velocity of the settling metal droplet, d_m is the diameter of the metal droplet, ρ_m is the density of metal droplet, ρ_s is the density of molten slag, μ is molten slag viscosity and g is gravity.

The separation velocity between metallic particle and slag is inversely proportional to slag viscosity according to Eq.(2), i.e. a lower viscosity which corresponds to a faster separation velocity. However, it is necessary to consider not only the separation velocity but also the retention time of iron collector in slag in order to achieve higher recovery rate of palladium according to the experiment results in Table 1. When the initial value of C/S is 0.3, the recovery rate of palladium in each group is less than 90%. This might be attributed to the high viscosity of molten slag that is difficult to maintain good fluidity for improving the collision frequency of iron and

palladium particles, eventually leading to the poor recovery effect. Then, when the C/S increases to 0.5, the slag viscosity decreases and reaches a reasonable value of 0.5~1.0 Pa·s. The slag with this viscosity keeps a good fluidity, which is not only suitable for separating ferroalloy from slag^[49], but also can ensure the collision frequency and residence time for fully collecting palladium. As C/S is 0.5, the content of waste catalyst and MgO is 30wt% and 8wt%, respectively, the optimal recovery rate of palladium is obtained, as high as 99.17%. However, the viscosity decreases continuously with further increase of C/S, and the lower viscosity is not conducive to the collecting behavior of iron due to the fast settlement. This eventually contributes to a decline in palladium recovery rate. Further addition of CaO has a negative effect on palladium recovery because the excessive CaO can increase the melting point of the slag and reduce the phase separation between the slag and alloy. In addition, excessive CaO can also increase the solubility of platinum group metals in the very basic slags^[50-52]. Therefore, the C/S ratio of the slag should be strictly controlled in the smelting process. Furthermore, the above analysis also shows that increasing the collision frequency of iron and palladium particles in the collection process is important to improve the recovery rate. It reminds us that strengthening techniques such as cavitation impinging stream and ultrasound will have potential application in the metal recovery field.

2.3 Dependence of smelting temperature on palladium recovery

The temperature is an important factor on physicochemical properties of molten slag system, which affects the smelting process directly^[30,49]. So, the temperature dependence of viscosity of slag system was firstly investigated when the C/S of slag was fixed at 0.5, and the results are shown in Fig.5. It is observed that both the measured and calculated viscosity obviously decrease from about 5.0 Pa·s to 0.2 Pa·s with increasing temperature from 1673 K to 1973 K, and the tendency of the decrease gradually diminishes with subsequently increasing temperature. This is because a higher smelting temperature can lead to more silicate network to be broken, resulting in the depolymerization of complex ion units in the

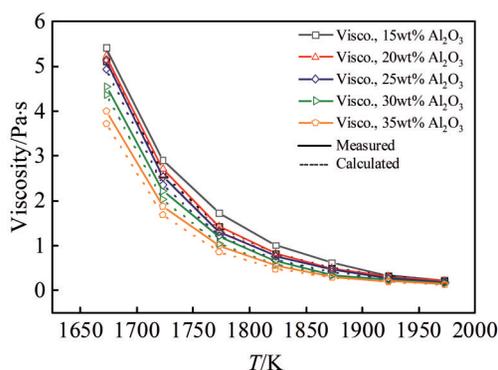


Fig.5 Temperature dependence of slag viscosity under different Al_2O_3 contents at C/S=0.5

slag. Usually, a higher degree of structural ion unit polymerization corresponds to a high viscosity in the melted slag system. In addition, the viscosity shows a decreasing tendency with increasing mass fraction of Al_2O_3 in slag system at a fixed temperature. Undoubtedly, it is of great practical significance to strictly control temperature in the smelting process.

In order to obtain an effective recovery of palladium, as well as to achieve an energy efficient process, the smelting temperature should be investigated and optimized by the experiment. In this work, the temperature range of 1673~1923 K was used in optimization experiments according to the liquidus isotherms diagram of slag system and empirical temperature from Ref.[28,30,49]. The other fixed conditions of optimization experiments are C/S=0.5, smelting time=1 h, and the result is shown in Fig.6.

It is observed that the recovery rate of palladium increases significantly with the increase of smelting temperature from 1673 K to 1823 K. This may be due to the fact that the high smelting temperature is conducive to the silicate network to be broken, resulting in the depolymerization of complex units in the molten slag. Therefore, it is consistent with the results in Fig.5 that the viscosity decreases with increasing temperature. So, the fluidity of molten slag is improved with rising temperature, which further enhances the sedimentation and diffusion of metallic particles^[28]. As a result, the palladium can be effectively collected^[1,53,54]. However, further rising temperature from 1823 K to 1923 K indicates an inhibiting effect on the palladium recovery, because the viscosity of molten slag excessively decreases with increasing the temperature, resulting in part of collectors to settle down before adequate palladium is collected. Thus, the appropriate smelting temperature in this study is fixed at 1823 K, and a high palladium recovery rate up to 99% is obtained when the content of waste catalyst Pd/ Al_2O_3 in the initial material is about 30wt%. Moreover, the smelting temperature of 1823 K is lower than the reduction temperature of silicon dioxide to monatomic silicon, which is an effective solution to avoid the formation of Si-Fe phase in the alloy.

2.4 Glass slag and ferroalloy from optimal experiment

Based on above analysis, the optimal smelting process was

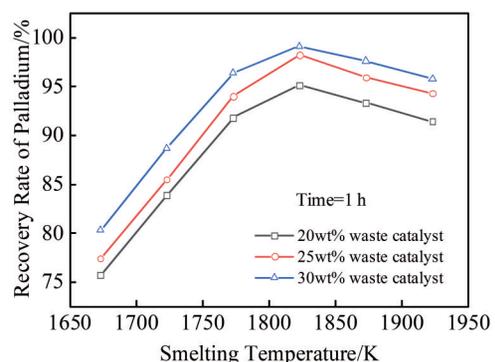


Fig.6 Influence of smelting temperature on recovery rate of palladium at C/S=0.5

conducted under the following conditions: the mass fractions of waste catalyst and MgO in the initial material are 30wt% and 8wt%, respectively, the C/S is 0.5, and the smelting temperature and time are 1823 K and 1 h, respectively. Then, the produced glass slag and ferroalloy were analyzed by a variety of analysis techniques such as XRF, ICP, XRD, and SEM-EDS. The detailed characteristics of glass slag and ferroalloy were obtained, and the palladium recovery efficiency was evaluated. Fig.7 shows the XRD patterns of the ferroalloy and glass slag. It can be seen from Fig.7a that the main metallic phase in the ferroalloy is Fe, and other phases such as FeSi₂ and FeSi can hardly be resolved from the XRD patterns due to the very low content.

The corresponding details of chemical composition for the ferroalloy and glass slag from three repeated experiments are listed in Table 2. It is observed that the mass fraction of palladium in the ferroalloy is about 0.80wt% which is less than inherent content in alloy Fe_{9.7}Pd_{0.3}. Therefore, Pd is dissolved in Fe phase and forms a solid solution. In addition, the collected palladium in ferroalloy is around 5 times as large as that in the waste catalyst and thousands of times as large as that in glass slag. The recovery rate of palladium is higher than 99% according to Eq.(1) calculated with the experiment data. Furthermore, the concerned silicon content in the ferroalloy is efficiently controlled by the present novel process, which is less than 1.0wt% and benefits to the subsequent refining process. Temperature is a significant factor to impact silicon content in the produced ferroalloy since the chemicals silicon dioxide and carbon react to form the monatomic silicon and the reaction is promoted by a rising

temperature^[55]. The above results illustrate that the overall effect of collection by the present novel process is obvious.

A stable and reasonable glass slag was produced in this study, which is environmentally friendly^[36-39,55] to meet the expectation of technological development, and further benefits to develop a novel idea on stabilization treatment of catalysts. It can be seen from Fig.7b that the slag is apparent in the amorphous phase, because there is no characteristic diffraction peak for crystalline phase but background signal from 20° to 35° for amorphous phase. This is also demonstrated by the macroscopic feature of slag. As shown in Fig.8, the slag is in dark green color and has typical glass properties such as transparency, light reflective, compact and smooth texture. The chemical compositions of glass slag obtained by XRF and ICP are shown in Table 2. The chemical composition is relatively stable before and after smelting. A small amount of ferrous oxide is detected in the glass slag, which might be attributed to the oxidation of iron collector. The content of palladium in glass slag of parallel experiment is very low, i.e. 3.78, 2.95 and 4.21 g/t, which is a verification of high efficiency of palladium collection by the present process. Moreover, from the tested data listed in Table 2, the composition of the glass slag is relatively simple, and the content of each component is basically determined. According to the previous literature, it is suitable for the preparation of some functional materials, for example, it can be reused further for synthesis of glass-ceramics by process treatment and the addition of nucleating agents^[40-42]. It also has other possible applications, such as raw materials for preparation of siliceous fire insulation slab and aggregates for road construction.

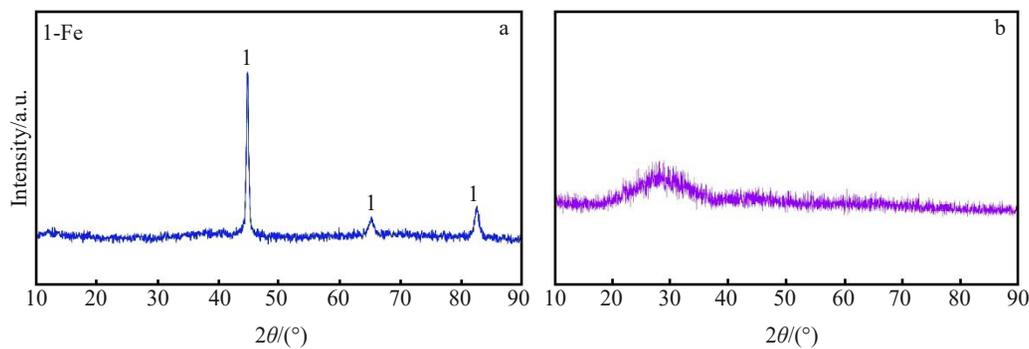


Fig.7 XRD patterns of the ferroalloy (a) and glass slag (b) from pilot-scale experiment

Table 2 Chemical compositions of ferroalloy and glass slag (wt%)

Experiment No.	Ferroalloy						Glass slag					
	Fe	Si	Cu	P	Pd	Others	SiO ₂	Al ₂ O ₃	CaO	MgO	FeO	Pd (g/t)
1#	96.88	0.83	0.71	0.40	0.79	0.39	40.62	30.03	20.76	8.07	0.23	3.78
2#	96.27	0.69	0.89	0.35	0.80	1.00	41.04	29.68	20.35	8.11	0.35	2.95
3#	95.83	0.94	0.82	0.52	0.76	1.13	40.11	30.72	19.83	7.91	0.19	4.21



Fig.8 Macroscopic feature of glass slag

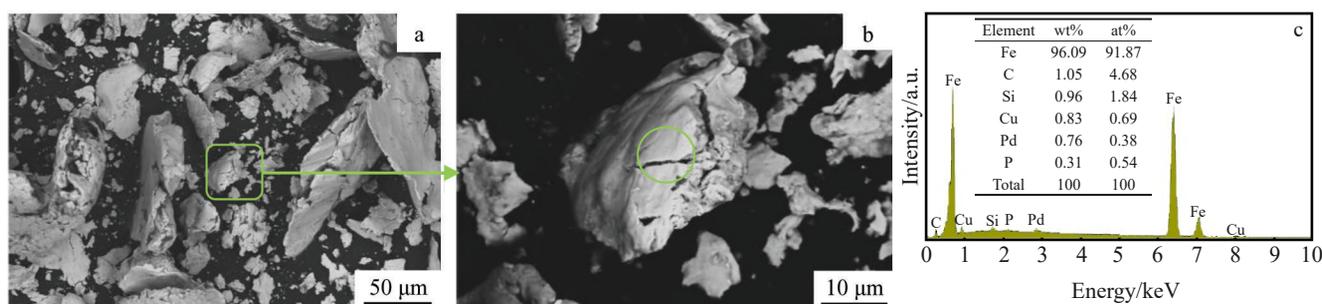


Fig.9 SEM images (a, b) and EDS results (c) of the ferroalloy from optimal smelting experiment

corresponding mass fractions are 96.09wt% , 1.05wt% , 0.96wt% , 0.83wt% , 0.31wt% and 0.76wt% , respectively, generally in agreement with the results listed in Table 2. Carbon in the ferroalloy mainly comes from graphite crucible, which is the greatest disadvantage of using graphite crucible in this process. The content of silicon in ferroalloy is less than 1.0wt%, again proving that the content of silicon in ferroalloy is effectively controlled. These above results further confirm a high efficiency of collection by the novel process.

3 Conclusions

1) Smelting-collection technology can be used to recover palladium from waste catalyst. A critical and reasonable composition of SiO_2 - CaO - Al_2O_3 - MgO quaternary glass slag is proposed for the novel process. The effects of binary basicity C/S, smelting temperature, as well as viscosity of molten slag on recovery palladium are evaluated.

2) The optimal viscosity of the slag system for palladium recovery is about 0.6 Pa·s at the smelting temperature 1823 K, the corresponding mass fractions of SiO_2 , CaO, and MgO in the quaternary slag system are about 41.3wt%, 20.7wt%, and 8.0wt%, respectively, the binary basicity C/S ratio is 0.5, and the added waste Pd/ Al_2O_3 catalyst in mixture is 30.0wt%. The slag from the smelting experiment is amorphous and has apparent macroscopic features of glass. The residual palladium content in the glass slag is very low and all the detected values are less than 4.50 g/t.

3) The collected palladium in ferroalloy is about 0.80wt% which is around 5 times larger than that in the waste catalyst

Fig. 9 shows the SEM images and EDS spectrum of the ferroalloy from the optimal experiment. It can be seen from Fig. 9a and 9b that no obvious inclusions, especially oxides from slag, are observed in the ferroalloy particles with varying sizes under different magnifications. This illustrates that the ferroalloy and glass slag are well separated in the smelting process. At the same time, the consistent color on the surface of the ferroalloy particles indicates that the composition of the alloy is relatively uniform. The random area marked with circle in Fig. 9b is chosen for elemental analysis by EDS and the results are shown in Fig. 9c. Six main elements of Fe, C, Si, Cu, P and Pd are contained in the ferroalloy and their

and thousands of times larger than that in glass slag. So, with the waste Pd/ Al_2O_3 catalyst used in this study and the optimal process conditions, the recovery rate of palladium can reach 99%. The concerned silicon content in the ferroalloy is less than 1.0wt%, which is efficiently controlled by the present novel process and benefits to the subsequent refining process.

4) The glass slag properties can obviously influence the melt fluidity and even the palladium recovery. Due to the strong effect of cavitation impinging stream on fluidity, its potential application in increasing melt fluidity to further improve metal recovery rate and efficiency will be carried out in the subsequent exploration experiment.

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玻璃渣性质对熔炼富集法回收废催化剂中钯的影响

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摘要: 利用热化学软件FactSage6.4计算了SiO₂-CaO-Al₂O₃渣系的等温相图, 进而通过固定辅料MgO的含量为8% (质量分数, 下同) 并控制Al₂O₃含量低于35%, 可以得到合理的玻璃渣系液相区温度和矿物学物相组成。采用旋转柱体法和模拟计算相结合的方法研究了温度、二元碱度 w_{CaO}/w_{SiO_2} 和Al₂O₃含量对SiO₂-CaO-Al₂O₃-MgO熔渣黏度的影响。依据单因素实验结果可知, 随温度逐渐升高、Al₂O₃含量由15%增加至35%以及二元碱度由0.3增加到1.0, 熔渣粘度呈减小的变化趋势。通过以铁作为捕集剂的熔炼实验可知, 钯的回收率随着废催化剂在物料体系中质量分数的增加而增大, 但随着持续增大二元碱度和升高温度, 其先增大而后减小。采用选取的Pd/Al₂O₃废催化剂和实验优化后的玻璃渣组分进行回收实验, 即Al₂O₃和MgO含量分别约为30%和8%、二元碱度为0.5, 钯的回收率可达99%, 玻璃态尾渣中钯的残留量小于4.50 g/t。

关键词: 废催化剂; 二次资源; 玻璃渣; 回收钯; 火法冶金

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