Recovering Palladium from Chloridizing Leaching Solution of Spent Pd/Al_2O_3 Catalyst by Sulfide Precipitation

Qian Li, Qiang Zou, Bin Xu, Yongbin Yang, Xuefei Rao, Long Hu and Tao Jiang

Abstract The recovery of palladium from the chloridizing leaching solution of spent Pd/Al_2O_3 catalyst was studied mainly by the sulfide precipitation tests and chemical composition analysis, and the relevant mechanism was also investigated in this paper. Results showed that when NaOH was previously added to adjust the leaching solution to pH increasing from 1.21 to 4, the recovery of palladium was nearly 100% whilst the dosage of precipitant Na_2S decreased by 75% comparing with direct precipitating by Na_2S solution without previously adjusting the initial pH. However, at $pH > 11.0$, the excessive addition of NaOH resulted in the formation of some $Pd(OH)_2$ from $[PdCl_4]^{2-}$, then the recovery rate of palladium was 98.18%. When the palladium lixivium concentration is too low or the sodium sulfide concentration is overhigh or the adding rate of sodium sulfide solution is too fast, $[PdCl_4]^{2-}$ could be transformed into soluble $[PdS_2]^{2-}$ because of partial over-dosage of sodium sulfide. Under the appropriate control of the above three factors, nearly 100% of palladium could be recovery successfully.

Keywords Palladium · Spent catalyst · Extraction · Sulfide precipitation

Introduction

Palladium is one of the longest known and most studied of the six platinum group metals, a reflection of its abundance and consequent availability. The main uses of palladium are in the electronics and electrical industries, in circuitry and in dental alloys. It finds many catalytic applications in industry, as well as in diffusion cells for the synthesis of hydrogen, and in automobile catalysts [1, 2]. The catalytic ability of palladium is of considerable industrial importance, so the demand for palladium has been increasing in recent years [3]. However, because of the

---

Q. Li (✉) · Q. Zou · B. Xu · Y. Yang · X. Rao · L. Hu · T. Jiang
School of Minerals Processing & Bioengineering,
Central South University, Changsha 410083, Hunan, China
e-mail: csuliqian@126.com

H. Kim et al. (eds.), *Rare Metal Technology 2017*,
The Minerals, Metals & Materials Series,
DOI 10.1007/978-3-319-51085-9_14

continuous adsorption of reactive solvents on the palladium catalyst surface and the loss of metal or active component during use, the catalytic performance of palladium catalyst gradual failure [1, 4]. As a result, the waste catalysts containing palladium accumulate continuously, and not only huge waste of palladium resources but also possible environmental pollution will be caused. Hence, it is urgent to recycle palladium from the spent catalysts, which can lower the production cost and raise the utilization rate of palladium as well as avoid unnecessary environmental pollution [5, 6].

The spent Pd/Al_2O_3 catalyst with Al_2O_3 as carrier used in oil chemical industry was an important resource for recovering palladium. Currently, the palladium in the spent Pd/Al_2O_3 catalyst is usually pretreated by oxidative roasting—acid leaching into leachate, often a chloridizing leaching solution. Various methods mainly including precipitation, solvent extraction, displacement, ion exchange and hydrolysis, have been used to separate palladium from the leachate. Among them, the precipitation method has been used most extensively in industrial production [3, 7]. Wada once pointed out that palladium could be completely precipitated by H_2S under cold state and in faintly acidic conditions [8]. Later, Beamish designed the technological process for separating palladium using H_2S [9]. However, the usage of H_2S cannot be controlled easily and severe co-precipitation of palladium with aluminum ion is accompanied. Hence, the separation effect is unsatisfactory. It was researched by Taimni et al. [10] that a large amount of sodium sulfide solution could be used to convert palladium complex into its $[PdS_2]^{2-}$; then acetic acid could be used to decompose the $[PdS_2]^{2-}$ of palladium into insoluble precipitate of palladium sulfide, achieving an effective separation of palladium from the leachate.

In this paper, sulfide precipitation with Na_2S was adopted to recover Pd from the chloridizing leaching solution of spent Pd/Al_2O_3 catalyst. The various precipitation behaviors of palladium with concentration of Pd and Na_2S as well as the addition method, pH, temperature and agitation speed were studied systematically, and the relevant mechanism was also discussed.

Experimental

Physical and Chemical Properties and Components of Lixivium

The chloridizing leaching solution of palladium was provided by Kunming institute of precious metals. The palladium in the solution occurs in the form of H_2PdCl_4. Contents of various elements in the lixivium are shown in Table 1. In H_2PdCl_4 solution, palladium content was 44 mg L^{-1} but many other impurities also existed. The existence of impurities would influence the precipitation effect and dosage of sodium sulfide for palladium to some extent. Particularly, Al was the major impurity element in lixivium and its content reached 3754 mg L^{-1}.

Table 1 Content of elements in palladium leaching solution (mg L^{-1})

Element	Na	Mg	Al	Si	P	S	K	Ca
Content	124	15	3754	13.15	121	93	117	134
Element	Cr	Mn	Fe	Ni	As	Sn	Pb	Pd
Content	10	18	128	3.18	1.41	0.065	1.85	44

Reagent and Detection Method

(1) Sodium sulfide solution: Analytically pure (AR) reagent (molecular formula $Na_2S{\cdot}9H_2O$, molecular weight 240.19, colorless and transparent crystal) was used for preparation.

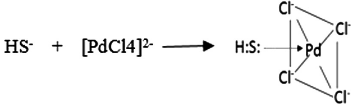
(2) pH measurement: Rex PHSJ-5 laboratory pH meter was used to measure pH value of the solution. E-201-D pH electrode assembly and T-820 °C temperature electrode were adopted. The measurement range of pH value is −2.000 to 18.000 and the fundamental error is ±0.002.

(3) Palladium content measurement: ICP-AES analysis was conducted to measure the components of lixivium. Palladium content in the filter liquor and precipitate was measured via atomic absorption spectrometry (AAS). The lower limit of analysis is good.

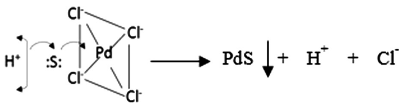
Experimental Principle

HS^- can be gained through hydrolysis of S^{2-}, and HS^- possesses quite strong electron-donating ability. $5P_z$ of complex ion $[PdCl_4]^{2-}$ having a square planar structure is a vacant orbital. Owing to sulphophile affinity of Pd atom, HS^- will directly contact Pd atom, and a pair of electrons in S atom will transfer to Pd. As a result, the binding force of Pd on four Cl^- ligands is weakened. Hence H^+ and Cl^- will be decomposed, and PdS can be formed.

$$S^{2-} + H_2O \leftrightarrow HS^- + OH^- \tag{1}$$



(2)



(3)

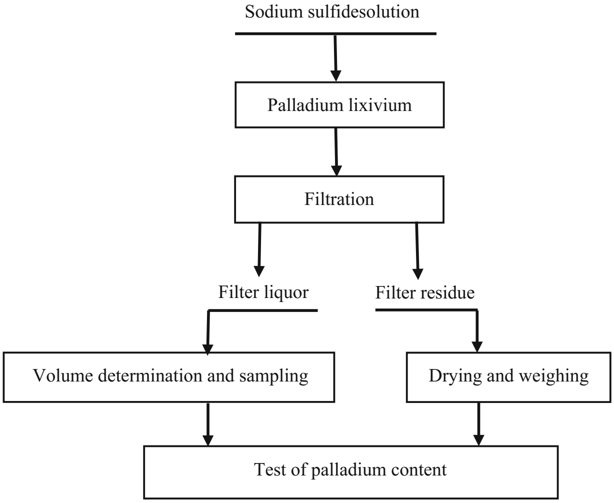


Fig. 1 Flow chart of test

Experimental Process

(1) 25 ml of palladium lixivium was taken out and put into a smaVll beaker of 100 ml;
(2) A rotor of 15 mm was used for stirring in the electromagnetic stirrer;
(3) An infusion tube which could be used to adjust the addition rate of Na_2S solution was utilized to fix the addition rate in the range of 0.1–0.5 ml s^{-1}, and the concentration of Na_2S solution 0.05–1.0 mol L^{-1};
(4) pH electrode was put into the beaker, and real-time measurement was conducted for pH;
(5) Filtration was conducted after the reaction, and the filter liquor was analyzed.

The flow chart of test is shown in Fig. 1.

Results and Discussion

Unless specified otherwise, the basic test conditions were dropwise addition rate 0.1 ml s^{-1}, agitation rate 1000 rpm, temperature 25 °C, initial pH 1.21, terminated pH 4.5, sodium sulfide concentration 0.5 mol L^{-1}, $[PdCl_4]^{2-}$concentration 44 mg L^{-1}.

Table 2 Leachate concentration on Pd recovery

Group	1	2	3	4
Leachate concentration of pd (mg/L)	44.0	22.0	14.7	11.0
The amount of sodium sulfide (ml)	8.0	4.0	2.7	2.0
Filtrate concentration of Pd (mg/L)*	0	0.1	0.1	0.2
Pd recovery (%)	100	98.18	98.18	96.36

"*" filtrate with 200 ml volumetric flask

Table 3 Effect of sodium sulfide concentration on Pd recovery

Group	1	2	3	4
Na_2S concentration (mol/L)	0.05	0.25	0.5	1.0
Termination pH	4.5	4.5	4.5	4.5
Na_2S amount (ml)	81.0	16.5	8.0	4.0
Pd recovery (%)	96.36	97.09	100	73.63

Effect of Lixivium Concentration on Palladium Precipitation

Changing concentration of Pd in leachate respectively group 1, 2, 3, 4 during the test to obtain the following data.

According to Table 2, with the decrease of palladium lixivium concentration, the dosage of sodium sulfide solution reduced proportionally. The recovery rate of palladium declined slightly with the decrease of lixivium concentration. As for the reasons, when lixivium concentration is excessively low, partial over-dosage of sodium sulfide will be caused. Hence, some of $[PdCl_4]^{2-}$ will produce thiofate of palladium, influencing precipitation of PdS. The reaction equation is indicated as follows:

$$[PdCl_4]^{2-} + 4HS^- \rightarrow [Pd(HS)_4]^{2-} + 4Cl^- \tag{4}$$

$$[Pd(HS)_4]^{2-} + 2OH^- \rightarrow [PdS_2]^{2-} + 2HS^- + 2H_2O. \tag{5}$$

Effect of Sodium Sulfide Concentration on Palladium Precipitation

Under the basic test conditions, changing Na_2S concentrations of the test to obtain the following data:

According to Table 3, with the rise of sodium sulfide concentration, the dosage of sodium sulfide diminished proportionally. When the sodium sulfide concentration (0.05 mol L^{-1}) was too low, the volume dosage of sodium sulfide was high

Table 4 Effect of terminated pH on Pd recovery

Group	1	2	3	4
Termination pH	3.8	4.0	4.5	5.0
Pd recovery (%)	98.18	100	100	100

and the reaction speed was relatively slow. When the sodium sulfide concentration (1 mol L^{-1}) was overhigh, $[PdCl_4]^{2-}$ would generate soluble $[PdS_2]^{2-}$, and thus the palladium precipitation would be incomplete.

Effect of Terminated pH During Reaction on Palladium Precipitation

The initial pH of lixivium was 1.21. When the stirring speed was 1000 rpm and the temperature was 25 °C, 0.5 mol L^{-1} sodium sulfide solution was added at the speed of 0.1 ml s^{-1}. The addition of sodium sulfide was stopped when the pH values reached 3.8, 4.0, 4.5 and 5, respectively. The measurement results are presented in Table 4.

According to Table 4, when solution pH was 4, palladium could be precipitated completely. When sodium sulfide was added continuously till pH became 5, PdS produced is still insoluble. When pH was 4, owing to the disturbance of aluminum ion, a large amount of colloid was produced, and the solution became brownish black gel. Consequently, the filtering separation was difficult. When pH was greater than 5, the formed colloid was destroyed, and obvious precipitate of black fine grains could be seen by the naked eye. If left to stand for 3 min the suspension would become obviously layered, and the separation effect was satisfactory.

Effect of Initial pH of Lixivium on Palladium Precipitation

As for the sample of Group 1, 0.5 mol L^{-1} HCl solution was used to adjust the initial pH decreasing from 1.21 to 0.5. As for the sample of Group 2, 0.5 mol L^{-1} NaOH solution was used to adjust pH increasing from 1.21 to 4.0, and the solution became milk white and cloudy due to the formation of insoluble aluminum hydroxide. As for the sample of Group 3, 0.5 mol L^{-1} NaOH solution was used to convert aluminum hydroxide into meta-aluminic acid; then the solution became clear again with a small amount of precipitate appearing in the bottom and pH shooting up to 11.0. As for the sample of Group 4, 0.5 mol L^{-1} NaOH solution was used to adjust pH to 12.0, and the solution property was the same as that of Group 3. The measurement results and content of elements in the filtrate are presented in Tables 5 and 6.

Table 5 Effect of initial pH on Pd recovery

Group	1	2	3	4
Initial pH	0.5	4.0	11.0	12.0
Termination pH	4.5	4.5	12.60	12.60
Na_2S amount (ml)	9.8	2.0	3.2	1.2
Pd recovery (%)	100	100	98.18	98.18

Table 6 Content of elements in the filtrate of group 2 and group 3 (mg L^{-1})

Element	Na	Mg	Al	Si	P	S	K	Ca
Group 2 content	1207	0.98	387	3.51	13.29	218	18	19
Group 3 content	3410	0	402	3.55	7.46	198	19	0
Element	Cr	Mn	Fe	Ni	As	Sn	Pb	Pd
Group 2 content	1	1.97	11	0.11	0.23	0.063	0.26	0
Group 3 content	0	0	0	0	0.25	0.053	0.26	0.1

According to Table 5, the palladium precipitation would not be affected under general acidic conditions. Moreover, palladium precipitation would also not be affected when NaOH solution was used to replace Na_2S solution to adjust pH to 4.0. Meanwhile, H_2S generation could be reduced, and the dosage of Na_2S solution would be decreased by 75% comparing with direct precipitating by Na_2S solution without previously adjusting the initial pH. This is primarily because that NaOH solution will precipitate impurity ions like Al^{3+}, Fe^{3+} and Ca^{2+}, etc. and meanwhile neutralize a large amount of H^+.

Under alkaline conditions, many aluminum ions existed in the form of meta-aluminic acid radical, and the dosage of Na_2S could be reduced by 85%. Meanwhile, no H_2S would be generated. However, the addition of a large amount of NaOH will result in the formation of some $Pd(OH)_2$ from $[PdCl_4]^{2-}$.

Effect of Adding Rate of Sodium Sulfide Solution on Palladium Precipitation

As for the samples of Group 1, 2 and 3, Na_2S solution was added into palladium lixivium at the rates of 0.1 0.2 and 0.5 ml s^{-1}, respectively. When the rate was higher, more bubbles could be produced. As for the sample of Group 4, palladium lixivium was added into 0.5 mol L^{-1} Na_2S solution, and the reaction was fast. When one drop was added, the entire system became brown and cloudy. The solution presented a colloidal and cloudy state after the reaction (Table 7).

Table 7 Effect of addition rate of Na_2S solution on Pd recovery

Group	1	2	3	4
Dropwise addition rate (ml s^{-1})	0.1	0.2	0.5	gigantic
Pd recovery (%)	100	98.18	89.09	27.27

Table 8 Effect of temperature on Pd recovery

Group	1	2	3	4
Temperature (°C)	25	50	80	100
Pd recovery (%)	100	100	100	100

Table 9 Effect of stirring speed on Pd recovery

Group	1	2	3	4
Stirring speed (rpm)	Without stirring	800	1000	1200
Pd recovery (%)	89.09	98.18	100	100

Under the conditions of maintaining lixivium concentration, Na_2S solution concentration and stirring speed unchanged, the recovery rate of palladium decreased slightly with the increase of adding rate of sodium sulfide solution. When lixivium was directly added into the sodium sulfide solution, the recovery rate of palladium was only 27.27%. This further shows that excessive sodium sulfide results in the generation of soluble thiofates of palladium. Hence, $[PdCl_4]^{2-}$ could not be completely precipitated in the form of PdS (Table 8).

Effect of Temperature on Palladium Precipitation

Under the temperature of 25 °C, palladium could precipitate completely. The rise of temperature had little influence on precipitation.

Effect of Stirring Speed on Palladium Precipitation

The stirring speed was related to the concentration of palladium lixivium and sodium sulfide as well as the adding rate of sodium sulfide solution, only 89.09% of palladium recovery percent without stirring, this is related to the generation of thiofate of palladium, so it was better to control the stirring speed within 1000 rpm (Table 9).

Conclusions

(1) The main controlling factors influencing precipitation of palladium from its lixivium as palladium sulfide is pH. When terminated pH during reaction is in the range of 4–5, it can precipitate completely. However, when pH was less than 4.5, the filtration is difficult due to the generation of colloid. Therefore, the optimal terminated pH should be about 4.5. After complete precipitating in the form of PdS, the generated precipitate is still insoluble even if excessive sodium sulfide is added.

(2) Under alkaline conditions of $pH > 11$, most palladium complex ions can precipitate in the form of PdS with little loss of palladium as $Pd(OH)_2$, and no H_2S will be produced. A large amount of NaOH was consumed previously, but the sequent dosage of sodium sulfide can be reduced by 85%.

(3) When the palladium lixivium concentration is too low or the sodium sulfide concentration is overhigh or the adding rate of sodium sulfide solution is too fast, partial over-dosage of sodium sulfide will be caused easily, but $[PdCl_4]^{2-}$ will be transformed to soluble $[PdS_2]^{2-}$ inevitably. In this situation, the precipitation of palladium is affected severely.

(4) In order to eliminate the influence of aluminum ion and reduce the generation of H_2S, NaOH can be used in advance to adjust the pH of palladium lixivium to 4.0. Hence, palladium can precipitate completely, and the dosage of Na_2S will be reduced by 75%.

Acknowledgments This work was financially supported by National Natural Science Foundation of China (Grant No. 51574284), National Science Foundation for Distinguished Young Scholars of China (Grant No. 51504293), Science and Technology Program of Yunnan (No. 2013IB020).

References

1. I.J. Ferrer et al., An investigation on palladium sulphide (PdS) thin films as a photovoltaic material. Thin Solid Films **515**(15), 5783–5786 (2007)
2. D.S.A. Cotton, *Chemistry of Precious Metals* (Chapman and Hall, London, UK, 1997)
3. W. Xu et al., Tailoring supported palladium sulfide catalysts through H2-assisted sulfidation with H_2S. J. Mater. Chem. A. **1**(41), 12811–12817 (2013)
4. A.A. Zirka, A.V. Mashkina, Liquid-phase hydrogenation of thiophenes on palladium sulfide catalysts. Kinet. Catal. **41**(3), 388–393 (2000)
5. A. Birri et al., Allyl palladium dithiocarbamates and related dithiolate complexes as precursors to palladium sulfides. J. Organomet. Chem. **692**(12), 2448–2455 (2007)
6. C. Fontàs, V. Salvadó, M. Hidalgo, Selective enrichment of palladium from spent automotive catalysts by using a liquid membrane system. J. Membr. Sci. **223**(1–2), 39–48 (2003)
7. R.S. Marinho, J.C. Afonso, Recovery of platinum from spent catalysts by liquid–liquid extraction in chloride medium. J. Hazard. Mater. **179**(1–3), 488–494 (2010)

8. J. Chen, Mechanism of sodium sulfide reacting with tetrachloropalladate and its application —I: quantitative precipitation of palladium by sodium sulfide. Precious Metals **1**(1), 7–15 (1980)
9. F.E. Beamish, A critical review of gravimetric methods for determination of the noble metals—II. Talanta **13**(6), 773–801 (1966)
10. I.K. Taimni, S.N. Tandon, Thermolysis of sulphides precipitated by sodium sulphide: sulphides of selenium, tellurium, gold, platinum, ruthenium, lead, bismuth, cadmium, silver, palladium and indium. Anal. Chim. Acta **22**(1), 553–557 (1960)