A Novel Technology for Rapid and Efficient Dissolution of Metallic Rhodium

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Abstract: The rapid and efficient dissolution of metallic Rh or Rh-base alloy scraps was recognized as a difficult technical problem in the circle of platinum group metals. Generally, the methods to dissolve these scraps include the high-temperature chlorination, fragmentation through alloying with Al, and melting with $NaHSO_4$，which possess a series of disadvantages, such as lower dissolution percentage (usually, less than 30% for one time dissolution), longer period, serious environmental pollution and larger consumption of energy and chemicals. The special crystal structure, which is chemical inert, on the surface of metals and some kinds of inert oxides formed on the surface may be the seasons for the difficult dissolution of crude Rh or Rh-base alloy scraps. A new process for rapid and efficient dissolution of crude rhodium was introduced in this paper. It consists of ① changing chemical reaction activation of precious metals by smelting matte and activated metals; ② separating base metals through acid dissolution and then filtration; ③ dissolving of Rh by directly addition of solid oxidants in HCl solution. The Rh dissolution percentage of more then 99% for one time dissolution could be reached in 24~48 hours. The concentration of Rh in the solution of base metals was less than 0.0005 g/L. This method is note for its rapid and efficient, more simples, less consumption of energy and chemical reagents and friendly environment. The recovery ratio of Rh for the whole process was >99%.

Key words: metallurgical technologies; platinum group metals; dissolution of Rh or Rh-base alloy
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一种快速高效溶解粗金属铑的新技术

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摘 要：高效快速的溶解金属铑或铑基合金废料，一直是铂族金属冶金中人们公认的技术难题。通常使用的高温氯化，熔铝碎化，$NaHSO_4$ 熔融等方法，有一次溶解率很低(一般不到 30%)，需反复多次处理，周期很长，金属损失大，环境污染严重，能源及试剂消耗大等缺点。金属表面呈化学惰性的结晶结构及可能形成某种惰性氧化物，是难溶的原因。针对粗金属铑（含 Rh 85.78 %）研究了高效快速溶解的新技术：① 用熔锍及活性金属转态活化；② 酸溶及过滤分离贱金属溶液；③ HCl 溶液中直接加固体氧化剂溶解铑。在较短周期 (24~48 h) 内，铑的一次溶解率＞99%，贱金属溶液中 Rh 浓度＜0.0005 g/L，全过程铑回收率＞99%。

关键词：冶金技术；铂族金属；铑及铑合金的溶解

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1 The technical difficult problem recognized in the field of platinum group metal metallurgy

All the refining processes of platinum group metals should be carried out in aqueous solution, whether it is conventional selective precipitation and separation, or it is advanced solvent extraction. That is said that all the raw materials, including the precious metal concentrates produced from the extraction of PGM ores and obtained from extraction of the PGM secondary resources, should be dissolved efficiently in aqueous solution at first, then could be separated and refined. Therefore, the rapid and efficient dissolution of precious metals is an important stage in the precious metals separation and refining. Technologies for dissolution of precious metals were discussed in detail in the anthor's monograph *Metallurgy of Platinum Group Metals* [1].

It is well known that the chemical dissolution of precious metals is very difficult. Thermodynamically, in the 8 elements of precious metals, the dissolution of Au is the most difficult, ($AuCl_4^-+3e=Au+Cl^-$, E^{θ}_{298}=1.00 V). The second one is Ir ($IrCl_6^{3-}+3e=Ir+6Cl^-$, E^{θ}_{298}=0.86 V). The third one is Pt ($PtCl_4^{2-}+2e=Pt+4Cl^-$, E^{θ}_{298}=0.579 V). Rhodium is the easiest soluble ($RhCl_6^{3-} + 3e = Rh+ 6Cl^-$, E^{θ}_{298}=0.44 V). However, it is exact opposite from the fact. In the six elements of platinum group metals, the dissolutions of Rh and Ir are the most difficult. Even though the strange oxidants (such as aqua regia and $HCl+Cl_2$, which can dissolve Au or Pt) are used, Rh and Ir can not be dissolved directly. Different pretreatment processes should be used before the dissolution.

Dissolution of metals belongs to the mechanisms of surface chemical reaction. The atoms on the surface of metals are dissolved layer by layer with chemical reagents producing oxidation-reduction reaction and changing the metals to ions. The reasons why the crude Rh or Rh-base alloys are very difficult dissoluble may be contributed to the following points. ① The crystal structures of atoms on the surface of Rh or Rh-base alloys are chemical inert. ② Some kinds of inert oxides are formed on the surface. Therefore, only these two points are overcome, the activity of Rh could not be improved. For example, the high grade precious metal concentrates (containing 9.8% Rh, Pt+Pd+Ru+Au=40%) are reduced by H_2 at 900℃ for one hour followed by dissolution with $HCl+HNO_3$ at 90 ℃ for 5 hours. The dissolution percentage of Rh was 14.6%. Comparatively, if the same concentrate was treated directly by $HCl+HNO_3$ at 90℃ for 5 hours, its dissolution percentage of Rh is only 8.5%. It shows that the reduction by H_2 could destroy the inert compounds and improve the dissolution activity of Rh. However, because the inert crystal structure on the metal surface has not changed, its dissolution rate is still very slow.

Some researchers believed that one influence factor on the dissolution of metallic Rh is the size[2]. Other researchers explained it from the view of atomic structures[3-4]. But all the research results are not ample enough and the completely acceptable solutions are not given.

2 Classification of the raw materials containing Rh and their pretreatment processes

2.1 The mineral materials containing Rh or Ir

For the precious metals concentrates, which consist of Pt, Pd and Au as the main components, and the content of Rh+Ir in it was 1/10 of the total amount of Pt+Pd+Au, a conventional technology was used to treat them including dissolution and selective precipitation for several stages. The method consists of ① treating the concentrates by $HCl+HNO_3$ or $HCl+Cl_2$ to dissolve Pt, Pd and Au; ② smelting with $NaHSO_4$; ③ leaching of Rh with dilute H_2SO_4; ④ smelting with Na_2O_2; ⑤ leaching of Ru and Os; ⑥ dissolving Ir_2O with $HCl+HNO_3$. The dissolution was an important step, although its dissolution percentage is not so satisfactory, it could be applied in industrial scale. For the mineral materials containing Rh or Ir with different grades a process including the smelt pretreatment by Al before the dissolution was developed[5]. For the advanced solvent extraction used

in the refining of precious metals, the dissolution of precious metals concentrates has not been a problem.

2.2 Pure metallic Rh powder

For the pure metallic Rh powder, chlorination at high temperature and high pressure[9-10] and the electro-dissolution with alternating current[11-12] are two new methods. For the former some special installations should be applied, as the result it is difficult to use this method in larger scale production. However, for the latter, it can be applied to directly produce high pure $RhCl_3$ with high recovery. Another advantage for the latter method is its simple technology. But at the present, the production scale is still not so large (several tens or several hundreds tones for per batch).

2.3 Crude Rh and Rh-base alloys

For the crude Rh and Rh-base alloys, the methods to dissolve them conclude ① high temperature chlorination-dilute HCl leaching[6-7]; ② fragmentation through alloying with Al-oxidizing leaching with strong acids; ③ smelting with $NaHSO_4$-leaching with water; and ④ smelting with hyperoxide of barium[8]. One key disadvantage for these processes is the lower dissolution percentage (<30%), as the result, it is necessary to dissolve for many times. It would cause the physical losses of Rh and Ir, and the longer dissolution period. The process of high temperature chlorination could lead to serious environment pollution. In addition, its heavy energy consumption and agents costs are two another disadvantages. For the process of $NaHSO_4$ melting-leaching with water, both the percentages of conservation and dissolution are very lower, and the valences of the ions in the solution are not suitable for the refining. So it is necessary to hydrolysis and re-dissolve for furthermore. For the process of fragmentation through the alloying with Al, because of the large different of the gravities of Al and Rh, the results of the fragmentation and dissolution are not so satisfactory. If Fe is used as the alloying element, the fragmentation should be carried out at 1500℃. It is very difficult to apply this process in industrial scale.

For crude Rh and crude Ir obtained from the extraction and concentration of the secondary resourse of precious metals and Rh-base alloys and Ir-base alloys, which are the most liable to be obtained and also have larger quantity. Their rapid and efficient dissolution has been the difficult problem recognized in the metallurgical circle. The metallurgists are paying a good attention to it.

A new technology to treat the crude metals, which have complex components, lower contents of precious metals, and several precious metals being co-exist, was introduced by the authors[13-14]. It consisted of capture-transform chemical reaction activation of precious metals. The dissolution percentages of precious metals were more than 99%. This process has been applied in industry effectively. The principle of this process is bases on the super strong infiltration, capture and transform of the valences abilities with sulfonium smelted. As the result, precious metals are concentrated and distributed in the matte as form of atoms. Then it is smelted with activated metals to form multi-metals alloys. Through the dissolution of base metals, precious metals become an easily to be dissolved activated metals with fine divided structure.

According to this principle mentioned above, a new transform of chemical reaction activation technology for rapid and efficient dissolution of crude metallic Rh was developed by the authors.

3 Experimental and results

3.1 The raw materials for experiments

A kind of crude Rh was used as the raw material. It contents 85.78% Rh and small amounts of Pt and Pd, 5 grams crude Rh was applied for each experiment.

3.2 The main results

3.2.1 The results of the transform of valences and activation synchro-experiments

The synchro-experiments were carried out by smelting (1250℃, 20 min) the raw material with No.1 or No.2 transform agents and No.3 activation agent, dissolving the base metals with acids to obtain the activated Rh concentrate, and dissolving Rh in HCl medium with No.4 solid oxidant. The results were listed in Tab.1.

Tab.1 Dissolution percentage of Rh for one time dissolution by the valence-transform-activation experiments

表 1. 转态-活化实验的铑一次溶解率

Transform agent / g	Activation agent / g	Covering residue / g	Insoluble residue / g	Content of Rh in the Insoluble residue / g	Dissolution percentage of Rh / %
No.1, 10	No.3, 30	Silicates	41	0.2018	98.07
No.1, 20	No.3, 30	—	43	0.2638	97.35
No.1, 20	No.3, 30	—	69.8	0.0624	98.90
No.2, 20	No.3, 30	—	35	0.3893	96.82

It was indicated that, by using these two kinds of transform agents and No.3 activation agent, the satisfactory effects of the transform and activation were be ensured and the dissolution percentage of >96% Rh was reached.

3.2.2 Effect of the different ratio of transform agent and activation agent

The experiments were carried out by different ratio of No.1 and No.2 agents with No.3 activation agent to obtain 0.25 L Rh solution. The results were shown in Tab.2.

For all the experiments listed above, the dissolution percentages of Rh were ~100% with the concentration of Rh in the residue being less than 0.1%.

Tab.2 The dissolution percentage of Rh for one time dissolution by different ratio of transform agent and activation agent

表 2. 不同比例的转态剂和活化剂条件下铑的一次溶解率

Transform agent / g	Activation agent / g	Covering residue / g	Concentration of Rh / (g/L)	Dissolution of Rh calculated from the solution / %	Insoluble residue / g	Concentration of Rh in Insoluble residue / g	Dissolution of Rh calculated from the residue / %
No.1, 15	No.3, 40	Silicates	16.56	96.53	21	0.061	~100
No.1, 20	No.3, 50	—	16.95	98.8	8	0.093	~100
No.1, 15	No.3, 40	—	17.5	102	8	0.029	~100
No.2, 20	No.3, 50	—	17.51	102.1	11	0.0223	~100

The differences between the dissolution percentages calculated from the solution and the residue ranged from 2%~3%, this indicated that the data from the analysis or the calculation were reliable.

3.2.3 The loss of Rh in the base metals containing solution

Solution from the dissolution of base metals by HCl is the only way of the loss of Rh for all the experiments. The concentrations of Rh by the analysis were in the range of <0.0001 to 0.0005 g/L with the highest value of 0.0014 g/L. Therefore, the loss of Rh in the base metals containing solution could be neglected.

3.2.4 Dissolution of Rh

In the metallurgy of precious metals, the dissolution of precious metals could be completed only in the HCl solution with the addition of strong oxidants, such as HNO_3, H_2O_2 and Cl_2 et al. If aqua regia ($HCl+HNO_3$) is used to dissolve precious metals, it would produce a large amount of acidic smoke and harmful nitrogen oxides causing the serous environment pollution. In addition, H_2O_2 is very expensive and easy to explode leading to the hidden dangers. The utilization ratio of chlorine gas pressured in steel sank is very low. Because of the escape of chlorine gas from the steel tank, the loss of the chlorine gas and the pollution cannot be avoided. Contrary, in this method No.4 solid oxidant was used to dissolve the activated Rh concentrate, thus, it has the advantages of simple, safety and less pollution. At the same time, this solid oxidant has stronger oxidation and lower cost.

3.2.5 The further recovery of Rh from the insoluble residue

The amount of the insoluble residue remained was not so large. Generally, it contains Rh of <0.1%, only the 0.01% of Rh in the raw material. Therefore, it could be combined with the raw materials to recover it.

3.2.6 The technical safety and environment protection

In the tests of this process, no any suddenly burning and explode were happened. Only small amount of H_2S and HCl gases were escaped during the dissolution of base metals. Besides, a small amount of Cl_2 and HCl gases were also escaped during the dissolution of Rh. These two steps could be carried out in sealed chamber with condenser or connecting a negative pressure system, then absorbing with alkali solution. By using this method the environment pollution could be avoided.

4 Pilot experiments and industrial application

The raw material of 50 g (containing Rh 42.9 g) was combined with 200 g No.1 transform agent and 300 g No.3 activation agent to transform and activation for one time. Base metals were dissolved by HCl. The concentrate of Rh was dissolve by HCl+No.4 solid oxidant under heating to obtain Rh bearing solution 2 L. It contains (g/L): Rh 20.8, Pt 1.64, Pd 0.14. The dissolution percentage of Rh calculated from the solution was 96.99%. The insoluble residue amounts 60.28 g, containing (%) Rh 0.0247, Pt 0.0513, Pd 0.0097. The dissolution percentage calculated from the residue was ~100%. These two results calculated by these methods were basically identical.

The raw material containing Rh of 3 kg was treated by chlorination at middle temperature for four times with the dissolution rate of < 30%. 2250 g of undissolved residue was obtained, which contain Rh 71.6% and Pt 18.8%. However, this material was treated by the technology introduced in the present paper only for one time, 41.23 L solution containing precious metals could be obtained, in which the concentrations of Rh and Pt were 37.35 and 10.08 g/L, respectively. The dissolution rates of Rh and Pt reached to 95.6% and 97.8%, respectively by the calculation from the solution.

5 Conclusion

(1) With the studied technology of the rapid and efficient dissolution of Rh, the dissolution percentage of Rh for one time dissolution was over 99% in 24~48 h. All the technical index reached the advanced level.

(2) The characteristics of this process were ① the process of transform of chemical reaction activation-dissolution was very simple with short treatment period, higher efficient, less energy consumption, and less environment pollution; ② the loss of Rh in the base metals containing solution could be neglected, and the recovery ratio of Rh was over 99%; ③ the solid oxidant used in the dissolution of Rh is cheaper, high efficient and safe to use; ④ the other precious metals in the raw materials could be dissolved and recovered simultaneously.

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