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STUDY ON THE OPTIMAL CONTROL OF HIGH LEAD ANODE COPPER ELECTROLYSIS BASED ON PARALLEL FLOW TECHNOLOGY

With the continuous expansion of copper smelting scale, copper concentrate resources are in serious shortage, resulting in the utilization of low-grade complex copper concentrate, which leads to anode passivation in copper electrolytic refining process due to high impurity contents. Aiming at this problem, in order to stabilize the cell voltage and improve the overall efficiency of the electrolytic refining process when treating high impurity anode copper, the effects of additives, electrolyte free sulfuric acid and technological operation on the cell voltage change were studied based on the unique electrolyte feeding movement mode of parallel flow technology. The results showed that in order to stabilize the cell voltage of electrolytic high lead anode copper at high current density, it was suggested that the amount of bone glue should be 40-90 g/t, the amount of thiourea should be less than 100 g/t, and the concentration of free sulfuric acid should be 160-180 g/L.

Keywords: Low-grade; electrolytic refining; parallel flow technology; electrolyte feeding mode

1. Introduction

With the continuous demanding of copper world widely, the high-quality copper ore resources are continuously exhausting, and the copper smelters must choose low-grade copper ore for production to guarantee the cathode copper supply in the market. However, low-grade copper ores contain high contents of arsenic, antimony, bismuth, lead, nickel and other impurities, and parts of them gradually go into slag, flue gas during the smelting process and the remaining part enriches in the anode copper and finally goes into the electrolyte [1-3], resulting in floating anode slime and affecting the quality of cathode copper in turn.

In the electro-refining, the lead in the anode copper will react with the sulfuric acid in the electrolyte to form lead sulfate, which is less soluble, easy to stick on anode copper surface and form a layer, resulting the converting of Cu to Cu²⁺, and anode passivation [4] (Fig. 1). Thereby, this causes the increase of energy consumption and decline of copper quality [5,6]. Therefore, it is significant of avoiding of anode passivation (Fig. 2) in high efficiency production.

There is close relationship between cell voltage and anode passivation. In the copper electro-refining process, the cell voltage is normally controlled at the range of 0.25 V to 0.5 V. Once

the cell voltage is out of this range, it indicates passivation of some anode copper [7]. The main reason for anode passivation is the formation of dense oxide and other compound on anode surface, which inhibits the continuous oxidation dissolution of



Fig. 1. Anode copper with anodic passivation

¹ YANGGU XIANGGUANG COPPER COMPANY LIMITED, LIAOCHENG 252000, CHINA

² HARBIN ENGINEERING UNIVERSITY, COLLEGE OF NUCLEAR SCIENCE AND TECHNOLOGY, HARBIN 15006, CHINA

³ CENTRAL SOUTH UNIVERSITY, COLLEGE OF CHEMISTRY AND CHEMICAL ENGINEERING, CHANGSHA 410083, CHINA

* Corresponding author: 172301012@csu.edu.cn





Fig. 2. Anode copper without anodic passivation

the anode. The existing solutions include adding active ions [8] and regulating the process conditions [9], etc.

There were two methods for copper electrolysis, the traditional electrolysis includes short period conventional electrolysis with small polar plate and long period conventional electrolysis with large polar plate [10]. Permanent stainless steel cathode electrolysis includes KIDD method (an electrolytic copper technology developed at the Kidd Creek smelter of Falconbridge, Canada), ISA method (an electrolytic copper technology developed at Mount Isa's Townsville smelter in Australia) and OK method (an electrolytic copper technology developed at the Otokumpu company in Finnish) [11], which has the characteristics and advantages of high current density, small inter-electrode distance, low scarp rate and short cathode life. Permanent stainless steel cathode plate electrolysis technology is a revolutionary change in the history of copper electrolysis refining. Furthermore, continuous innovation is happening to its mechanization, automation level, product production capacity and quality optimization and other aspects in and outside China. In the early 21st century, Yanggu Xiangguang Copper independently developed the parallel flow electrolysis technology [12]. For traditional electrolysis, electrolyte is inlet from the upper part and outlet from the lower part of the cell or is inlet from the lower part and outlet from the upper part of the cell are the main feeding modes [13]. The electrolyte flows along the bottom and sides of the cell perpendicular to the plates, thus the flow rate is very small between cathodes and anodes [14]. The electrolyte feeding mode adopted by the parallel flow technology is that the electrolyte is fed the cell

from the lower side part of each cathode plate and flows upward along the cathode plate surface, which results effective wearing to the electrode surface, thus the thickness of the phase film layer on the electrode surface is decreased and the electrolyte, additives and temperature in the electrolysis system achieves an balanced state.

Due to its unique electrolyte feeding mode, the parallel flow technology effectively remitted problems such as the anode passivation, electrolyte concentration polarization, etc. in the conventional anode electrolysis process. With random current measuring between some cathodes by fiber optic current sensor [15] (Fig. 3), the current density is increased above 420 A/m^2 . In this paper, the parallel electrolyte feeding mode from the lower part of the cathode copper to avoid anode passivation and improve current density is described based on the parallel flow technology. The production process optimization and improvement of electrolysis efficiency is carried out with high lead anode copper with a lead content higher than 155% of conventional anode copper as research target. The selected anode copper is beyond the allowable range and prone to anode passivation. It is necessary to regulate the process parameters to avoid passivation.

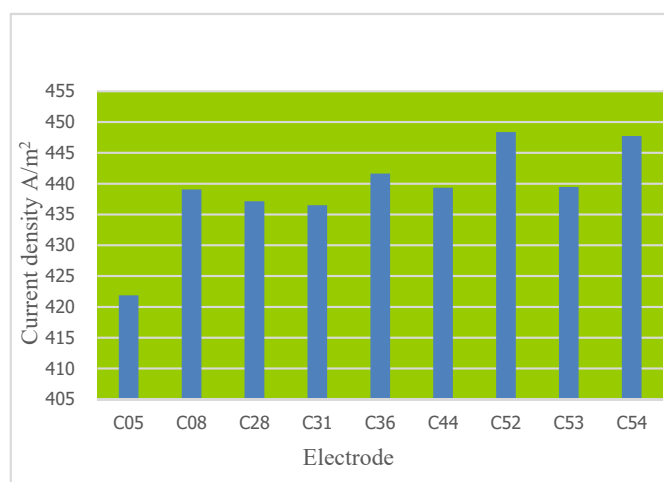


Fig. 3. Current density distribution between cathode electrodes

2. Experimental method

2.1. Experimental materials

The lead content in the anode copper is required to be less than 0.2 wt.% for traditional conventional electrolysis with current density between 180 A/m^2 and 280 A/m^2 . As can be seen from TABLE 1, the lead content of the anode copper for experiment is 0.51 wt.%.

TABLE 1

Content of elements in high lead anode copper for experiment, wt.%

Cu (%)	Pb (%)	S (%)	Fe (%)	As (%)	Sb(%)	Bi(%)	O(%)	Ni(%)	Zn(%)
99.05	0.51	0.0035	0.0046	0.086	0.016	0.11	0.064	0.016	0.008

2.2. Electrolysis experiment

The electrolyte was conveyed into the electrolytic cells by a variable- frequency circulating pump after passing through a plate heat-exchange system. The electrolyte was introduced to each cell through inlets to the lower part of the cathode plate along the horizontal direction. The temperature of the electrolyte was kept at 62-66°C, the electrolyte flowrate was 80-100 L/min, and the free acid concentration was 140-200 g/L. Bone glue and thiourea were continuously added to the electrolyte by a charging system to ensure constant additive concentrations. The dosage range of bone glue was 40 g/t ~ 110 g/t, and the dosage range of thiourea was 50 g/t ~ 120 g/t. The element composition of bone glue used in the experiment was (wt.%): C 5.0 ~ 50.0, H 6.5 ~ 7.5, N 15.0 ~ 19.0, O 20.0 ~ 23.5 and S 0.5. Surface crystallization quality of the cathode copper was experimentally controlled by monitoring the temperature and cell voltage. The electrolyte and cathode were sampled before and after each electrolysis cycle [16].

2.3. Characterization

The phase of cathode copper products was analyzed using a Japanese company TTR III X-ray diffractometer (XRD). The test conditions are: working voltage of 40 kV, working current of 250 mA, scanning rate of 10 Å/min, $\lambda = 0.15406$ nm.

3. Results and discussion

3.1. Influence of process parameters to electrolysis of the high lead anode copper

3.1.1. Influence of bone glue

Bone glue is the most widely used glue additive in copper electro-refining process. By adding bone glue, the growth rate of crystal nucleus can be effectively controlled so as to obtain cathode copper with fine grains and smooth surface [17-20].

Fig. 4 shows the relationship between the amount of additive bone glue and cell voltage. As can be seen from the figure, when the amount of bone glue is lower than 100 g/t, the cell voltage remains in the normal range of 0.25-0.5 V, indicating that the electrolysis is normal and there is no anode passivation. When the amount of bone glue is 100 g/t and 110 g/t, the cell voltage is 0.85 V and 0.90 V respectively, which exceeds the normal value, indicating that some anode copper in the electrolytic cell has been passivated. The main reason for anode passivation is that when the amount of additive bone glue is high, excess bone glue is absorbed on the surface of the anode plate during copper electrolysis, which reduces the dissolution activity and accelerates the generation of anode concentration polarization [21]. When the amount of bone glue is small, enough cathode polarization cannot be generated on cathode copper, and the

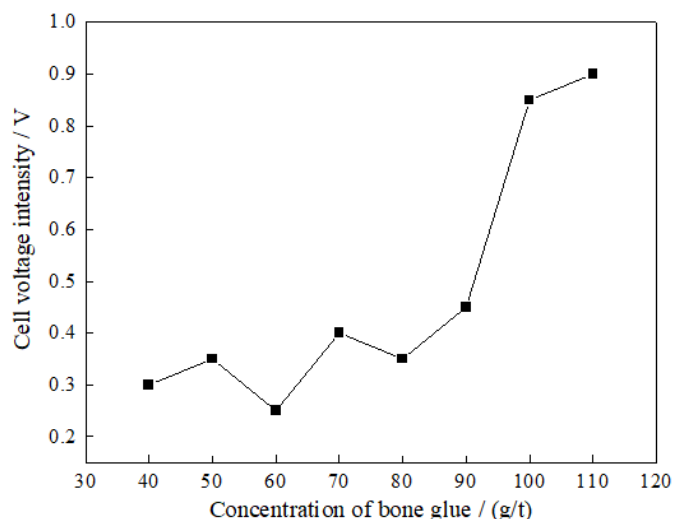


Fig. 4. Variance of the cell voltage intensity with the concentration of bone glue

grain growth rate is fast, resulting in poor cathode copper quality, which is also not desirable. Therefore, the optimal amount of bone glue in the production process under high current density is 40-90 g/t.

3.1.2. Influence of thiourea

Thiourea, a white crystal, is one of the additives commonly used in copper electro-refining [22]. The addition of thiourea can refine the crystallization, which is beneficial to the densification of the cathode plate surface.

Fig. 5 shows the relationship between the dosage of thiourea additive and the cell voltage. As can be seen from the change of the cell voltage caused by the change of thiourea dosage in the figure, when the thiourea dosage is less than 110 g/t, the cell voltage does not change much and is within the normal range of

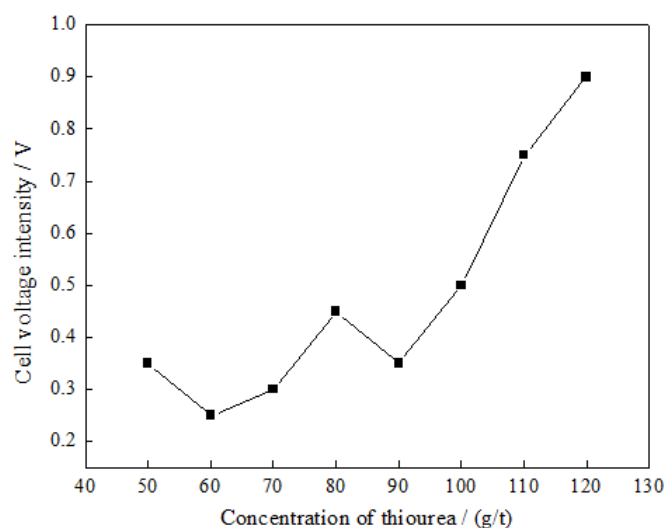


Fig. 5. Variance of cell voltage intensity with the concentration of thiourea

0.25-0.5 V. When the dosage of additive thiourea is 110 g/t and 120 g/t, the cell voltage exceeds the normal range, that is, the anode passivation occurs [23]. Therefore, the optimal thiourea dosage in the production process should be less than 100 g/t.

3.1.3. Influence of free sulfuric acid

Free sulfuric acid in the electrolyte has two functions: on the one hand, it can improve the conductivity of electrolyte. On the other hand, avoid disproportionation reaction due to cuprous sulfate hydrolysis and generate cuprous oxide [24].

Fig. 6 lists the cell voltages at several different concentrations of free sulfuric acid. When the concentration of free sulfuric acid is lower (≤ 150 g/L), the conductivity of electrolyte is poor and the cell voltage increases. When the concentration of free sulfuric acid is too high (such as >190 g/L), on the one hand, the anode slime generated at high sulfuric acid concentration is thicker and denser, which hinders the diffusion of copper ions from the anode surface and easily causes anode passivation. On the other hand, the high concentration of sulfuric acid reduces the saturation solubility of copper sulfate, and the copper sulfate crystal is easy to spread on the surface of anode copper, resulting in anode passivation. When the concentration of free sulfuric acid is controlled at 160-180 g/L, the electrolyte can be guaranteed to have good conductivity and the cell voltage can be controlled within a reasonable range (0.25-0.5 V). Therefore, under the experimental process conditions, the optimal concentration of free sulfuric acid is 160-180 g/L.

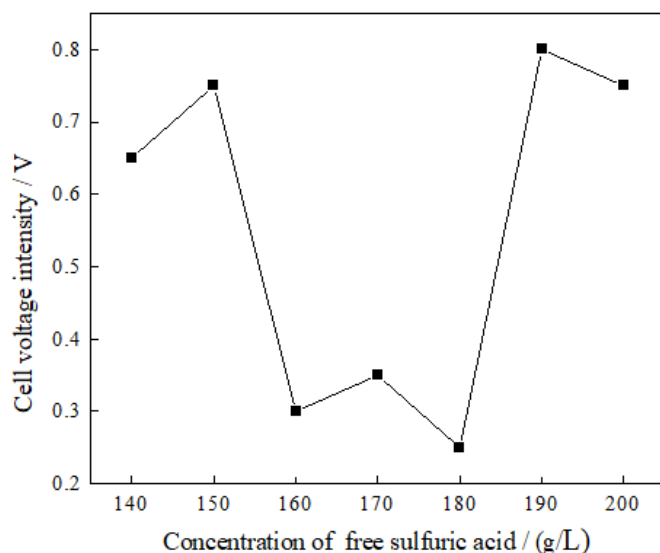


Fig. 6. Variance of cell voltage intensity with the concentration of free sulfuric acid

3.1.4. Influence of electrolyte temperature

The effective time of bone glue used in electro-refining is inversely proportional to the temperature [25]. That is, the higher the temperature of the electrolyte, the shorter the effective dura-

tion of the glue. Therefore, the temperature of the electrolyte should be controlled in a reasonable range. Under the conditions of this experiment, the temperature of the electrolyte should be kept in the range of 60-65°C.

3.1.5. Influence of the electrolyte circulating system

The current density of parallel flow technology is above 420 A/m². The anode dissolution rate accelerates with the increase of current density, which increases the formation trend of copper sulfate pentahydrate and cuprous oxide, accelerates the increase of thickness and density of anode slime layer, and results in anode passivation in the electrolysis process [26].

The traditional electrolyte circulation system uses a high pressure pump to send the electrolyte to the overhead tank, and then distributes the electrolyte to each cell through the overhead tank and the electrolyte distributor. Parallel flow technology eliminates the overhead tank, electrolyte distributor and heat exchanger in electrolyte circulation system, and directly uses variable frequency pump instead of high pressure pump to send electrolyte to each electrolytic cell, so as to meet the requirements of electrolyte flow rate [27]. By increasing the electrolyte circulation rate from 30 L/min to 95 L/min, copper ion diffusion is accelerated and the anode passivation is reduced.

3.2. Comparison of Electrolysis between High Lead Anode Copper and Normal Anode Copper

In order to obtain densely crystallized cathode copper (Fig. 7(b)), the growth rate of crystal nucleus should be controlled well in the crystallization stage of electrolysis process, which can produce crystals with fine grains and smooth surface quality, if the formation rate of crystal nucleus is too fast, it is difficult to form crystals (Fig. 7(a)). In addition, the cathode copper products in irregular shape caused by anode passivation doesn't conform to the surface quality requirements stipulated in the national Cathode Copper standard (Fig. 8), thus they can only be returned for melting and recasting, which causes more energy consumption, influences the completion of production plan and downgrades the productivity. The main problem caused by anode passivation is that surface quality defects are produced, and there is no obvious change in morphology. The content of main elements in cathode copper products meets the requirements in TABLE 2.

TABLE 2

Chemical composition of cathode copper produced by parallel flow electrolysis (wt.%)

Element	Cu	As	Sb	Bi	Pb
Content	>99.9935	<0.000050	<0.00010	<0.000050	<0.00010

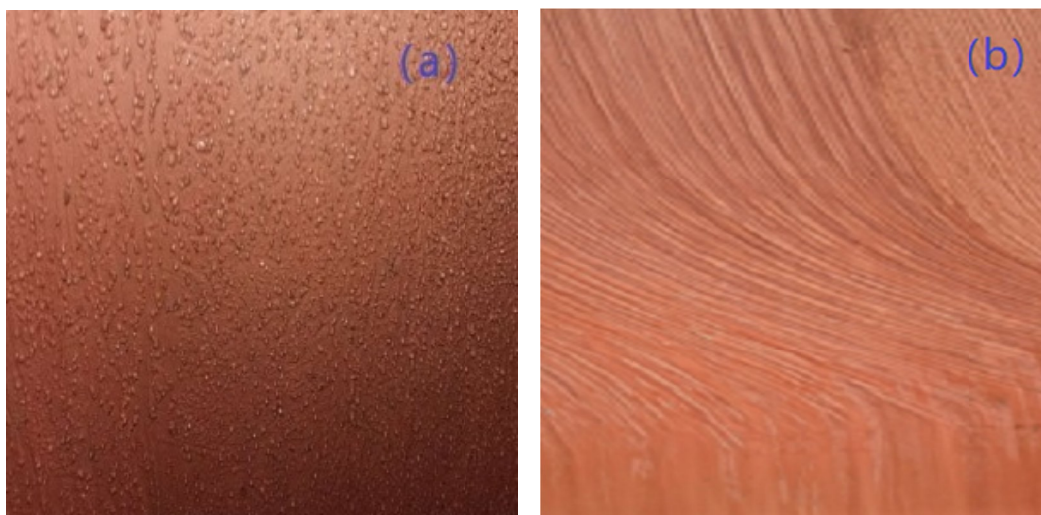


Fig. 7. Surface images of copper cathode taken (a) cathode copper with rough surface and (b) cathode copper with smooth surface



Fig. 8. Different morphologies of cathode copper products after electrolysis

3.3. X-ray diffractometer characterization of cathode copper

Fig. 9 is the X-ray diffraction pattern of certain sections of the cathode copper. In all four patterns, there are no diffraction peaks of other phases but only Cu diffraction peaks. It can be seen from the data in TABLE 3 that the relative intensity data and texture coefficient of diffraction peaks of sample a# are very close to the data of PDF card, indicating that the primary grains on the stainless steel cathode plate are disorderly in the spatial direction, that is, there is no preferential orientation nucleation phenomenon. The X-ray diffraction data of sample b# are consistent with the results of Lu Daorong et al. [26], that is, with the addition of thioureas, the growth of cathode copper has the

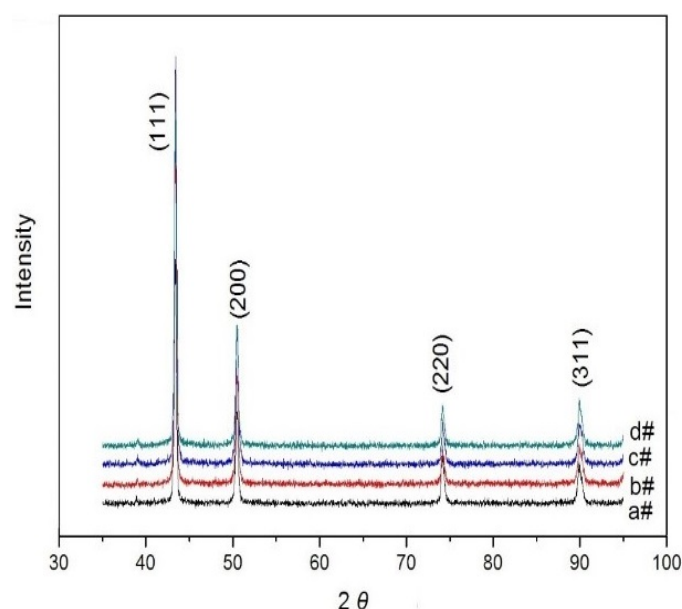


Fig. 9. X-ray diffraction pattern of cathode copper (a#) surfaces contacting with stainless steel cathode plate, (b#) surfaces inside the cathode copper in parallel with stainless steel cathode plate, (c#) surfaces perpendicular to the fine fringes and stainless steel plate, (d#) surfaces in parallel with fine fringes and perpendicular to stainless steel cathode plate

preferred orientation of [111] crystal direction, and the texture coefficient of [111] crystal direction is increased from 47.4% to 54.0% of the non-optimal orientation.

By comparing the texture coefficients of each crystal plane of cathode copper samples with different sections of b#, c# and d#, it can be seen that sample c# has the strongest [111] and [200] texture coefficients, indicating that the [111] and [200] dendrites along the fine fringe direction of cathode copper surface are the most developed. By comparing the crystal plane spacing of different crystal planes in each section, it can be found that the crystal plane spacing of c# sample is the smallest, while the crystal plane spacing of d# sample is the largest, which means that in the grain, the spacing of crystal planes perpendicular to fine

fringes is the smallest and the arrangement is the most compact, while the spacing of crystal planes perpendicular to stainless steel cathode plate and in parallel with the crystal plane of fine fringes is the largest and the arrangement is the most sparse.

TABLE 3

Parts of X-ray diffraction data of some sections

		PDF card	a#	b#	c#	d#
(111)	<i>d</i> (nm)	0.20871	0.20845	0.20838	0.20823	0.20840
	<i>I</i> / <i>I</i> ₀	100	100	100	100	100
	T.C. (%)	48.3	47.4	54.0	55.1	51.9
(200)	<i>d</i> (nm)	0.18075	0.18068	0.18060	0.18053	0.18065
	<i>I</i> / <i>I</i> ₀	49	50.4	44.7	45.4	47.5
	T.C. (%)	23.7	23.9	24.1	25.0	24.6
(220)	<i>d</i> (nm)	0.12781	0.12773	0.12769	0.12767	0.12771
	<i>I</i> / <i>I</i> ₀	28	28.7	15.0	14.2	18.2
	T.C. (%)	13.5	13.6	8.1	7.8	9.4
(311)	<i>d</i> (nm)	0.10899	0.10897	0.10895	0.10892	0.10895
	<i>I</i> / <i>I</i> ₀	30	31.7	25.6	21.8	27.2
	T.C. (%)	14.5	15.1	13.8	12.0	14.1

Note: T.C. is texture coefficient. [27], $T.C. = \frac{I_{hkl} / I_{0hkl}}{\sum (I_{hkl} / I_{0hkl})} \times 100\%$

4. Conclusions

- (1) To avoid anode passivation caused by bad processes such as reactions between additive and electrolyte copper ions, sulfate ions, chloride ions generating insoluble compounds to hinder the reaction between anode and electrolyte or the negative end of the dipole molecule pointing to the anode surface and be adsorbed on the electrode, the optimal amount of bone glue is 40-90 g/t, the amount of thiourea is less than 100 g/t, and the concentration of free sulfuric acid is 160-180 g/L under high current density (above 420 A/m²) through experimental verification.
- (2) The principle of the parallel flow technology is described. By feeding the electrolyte into the cell from the lower part of the cathode copper and change of the electrolyte circulation, the current density is improved and anode passivation is decreased. In the next step, we will fundamentally eliminate anode passivation by implementing automatic voltage measurement on the electrolysis cells to monitor the data in real time.
- (3) As the parallel flow technology is adaptive to the electrorefining of high lead anode copper and can significantly improve copper electrolysis capacity, it has good application value in the copper smelting industry.

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