DEVELOPMENTS IN PERMANENT STAINLESS STEEL CATHODES WITHIN THE COPPER INDUSTRY

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ABSTRACT

The ISA PROCESS™ cathode plate is characterised by its copper coated suspension bar, coupled with a blade employing austenitic stainless steel alloy 316L. The blade material has become the mainstay of the technology and has been closely copied by competing cathode designs. Improvement to the cathode plate design remains a key area for research, and ongoing developments by Xstrata Technology's ISA PROCESS™ have recently been commercialised. Two such developments are the ISA Cathode BR™ and ISA 2000 AB Cathode. The ISA BR cathode is a lower resistance cathode that has proven to enhance operating efficiencies. The AB cathode was designed to improve stripping inefficiencies in the ISA 2000 technology. These developments have now had time to mature and their long term performance will be discussed. Rising material costs and the desire to extend the operating boundaries of the standard 316L cathode plate has triggered a number of significant advances. These involve the use of different stainless steels as alternatives in some operational situations. The technical aspects and results of commercial trials on this development will also be discussed in this paper.

INTRODUCTION

The introduction of permanent stainless steel cathode technology was pioneered in the copper industry by IJ Perry and colleagues in 1978, with the introduction of the ISA PROCESS^{TM} in the Townsville Copper Refinery, Perry [1]. While a number of parallel processes have emerged since its introduction, ISA Process Technology (IPT) has continued to be the mainstay electrolytic copper process with consistent improvements and superior operational performance.

Following the introduction of the ISA 2000, recent developments that have been offered to the market are the ISA BR and AB cathode plate. The BR plate offers a low resistance electrode that has the potential to significantly reduce power costs. The AB cathode was introduced to the market to improve stripping performances particularly where tankhouses with the ISA 2000 technology were prone to frequent power outages.

A new development soon to be introduced into the market is the use of alternative steels for cathode plates. Rising costs and the desire to extend the operating boundaries of the 316L alloy triggered investigations into alternate stainless steel types and their application to various copper electrolytic processes. The steels tested have the potential to reduce the capital cost of the cathodes while still providing a technically sound cathode. Tests have been carried out in diverse operating environments from small low-cost electrowinning operations to intensively managed electro-refining plants.

ISA CATHODE BR^{TM} – "LOW RESISTANCE" PERMANENT CATHODE

BR Design

The BR cathode design extends the copper plating up to 55mm down the blade, compared to the standard ISA plate of 15-17mm. The extension of the copper plating reduces the amount of electrical resistance that exists between the copper plating and the solution line. This is achieved by reducing the distance the current has to travel through the stainless steel. The resistance of stainless steel is 74 μΩ.cm @ 50^0C compared to a value of 1.8 μΩ.cm @ 50^0C for copper.

The BR design can increase the average copper plating thickness from 2.5mm to 3.0mm. The increase in copper thickness increases the corrosion resistance of the plate. This is particularly advantageous in electrowinning applications where cathodes may be subjected to corrosive conditions.

Development of the BR cathode

Standard ISA cathodes, whilst superior in most aspects to alternate stainless steel cathode configurations have slightly higher resistance than solid copper hanger bar systems. While the lower resistance is attractive, deficiencies for some applications in the long term performance of the solid copper hanger bar were identified following a large scale trial at the Townsville Copper Refinery. Webb [2]

The initial development of the BR cathode, as reported by Webb [2], followed trials conducted to compare the performance of solid copper hanger bar cathodes and ISA PROCESS™ cathodes. These trails indicated that whilst ISA PROCESS™ cathodes gave higher current efficiencies of 2% to 2.4% (electro-winning and electro-refining respectively) the continuing market demand to produce copper more efficiently lead to the development of the lower resistance ISA cathode BR™.

Figure 1 – ISA cathode BR™

Additional Testing of the BR Cathode

In addition to the early work completed by Webb [2] the internal plate resistance of various cathode plates have been measured using a digital micro-ohmmeter at Townsville's Copper Refinery. To replicate cell conditions, cathode plates were plated with copper for a period of 24 hours then the resistance measured. The average plate resistances are shown in the graph below.

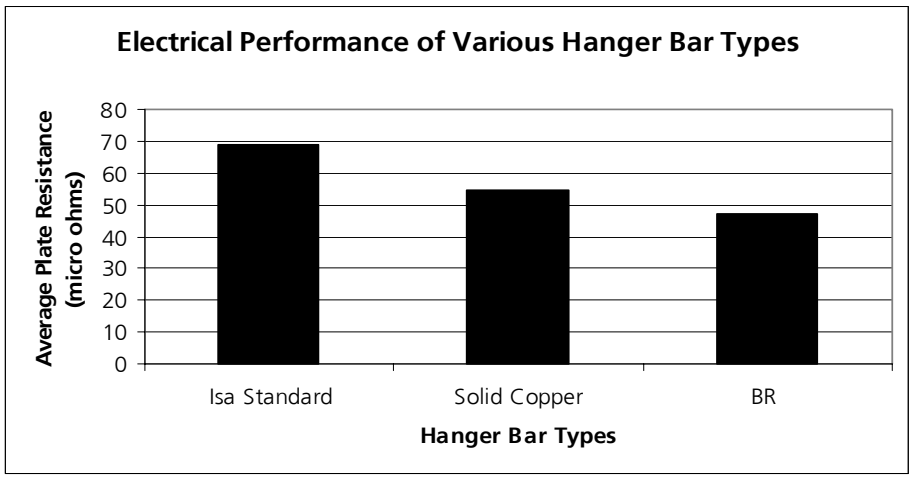

Figure 2 – Internal resistance of various hanger bar types

The measurements complemented Webb's [2] original work by confirming the ISA Cathode BR™ as the electrically superior plate, by exhibiting the lowest plate resistance.

Further operational measurements have been completed at other ISA PROCESS™ electrowinning facilities. All measurements confirm the previous work completed by Webb [2] at Compania Mineral Zaldivar showing a potential saving of US$100,000 per year in power costs could be achieved with the ISA Cathode BR™. This equates to a cost saving of approximately US$0.75 per tonne of copper produced.

Since the ISA BR™ cathodes introduction in the early 2000's, in excess of 106,000 BR configured plates have been produced, representing approximately 450,000 tonnes of copper per year. These plates have been installed in 6 plants in Japan, USA, Philippines and South America.

THE DEVELOPMENT OF THE AB CATHODE

The ISA 2000 Waxless System

To eliminate the need for wax as a bottom and side masking agent ISA PROCESS™ developed a waxless cathode design, now commonly known as the ISA 2000 technology.

The principle behind the waxless development lies within the 90° v-groove machined into it. This allows separation of the enveloped cathode into two separate sheets by the ISA PROCESS™ stripping machines. On a micro-scale, the copper crystals grow perpendicular to the cathode plate from opposing sides of the v-groove, causing them to intersect at right angles to each other. Where they intersect, a discontinuity in the structure is formed, resulting in weak zone, along which the copper splits.

Figure 3 details a microscope view of a copper cathode cross-section, taken from the v-groove region, magnified 10 times. The sample was polished and etched to show the copper crystal structure. The white lines indicate the orientation and direction of crystal growth.

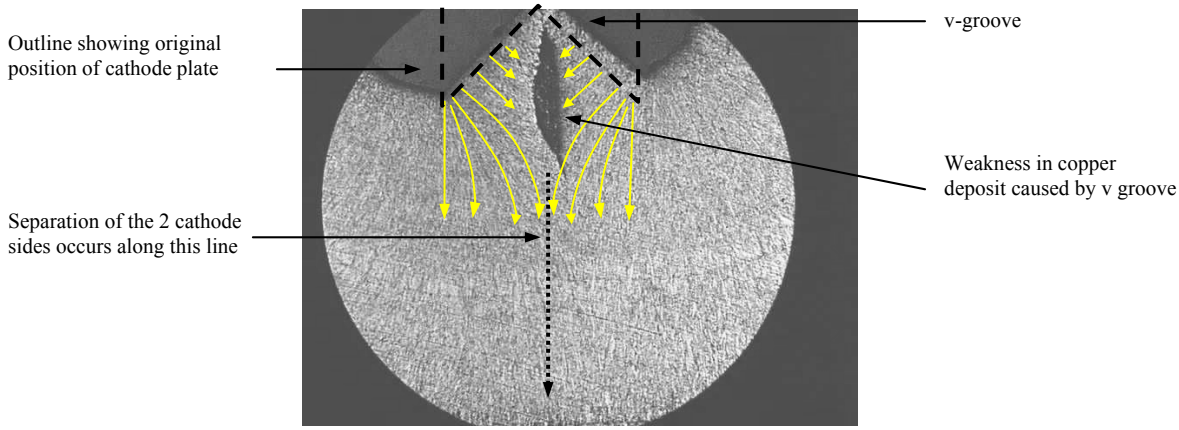

Figure 3 - Microscope view of cathode deposit cross-section in the v-groove region.

In addition to this effect it is believed in electrowinning facilities small gas bubbles (oxygen from the anodes) become trapped in the groove. This gas layer then serves as an insulating layer between the two growing faces.

The v-groove splitting mechanism combined with modifications in the stripping machines has been extremely effective in the separation of copper cathodes under most circumstances.

The AB Design

The AB cathode design has 45 degrees chamfered corners cut away from the bottom of the blade. The "v" groove runs the length of the blade and up the chamfered corners. The dimensions of the chamfered corners are 60mm x 60mm. These dimensions have been chosen to maximise the tearing action, whilst reducing the chances of bending the cathode corners or producing a ropey edge that would potentially entrap falling slimes. The tearing action produced by the corner chamfers initiates the split of the copper sheets and improves splitting if lamination has occurred.

The edgestrips designed for the AB cathode are a cross slot edgestrip with a moulded bottom plug. The internal dimensions of the plug have been specifically designed for the AB cathode and allow the edgestrip to fit securely onto the AB plate to prevent nodule growth.

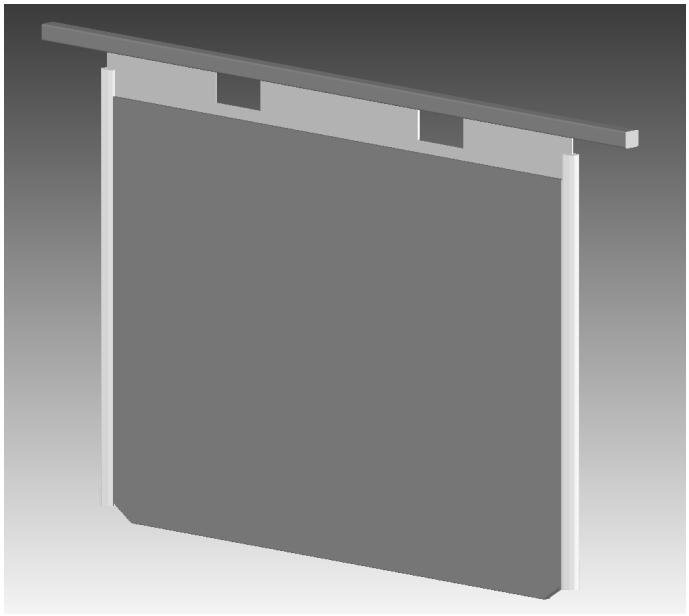

Figure 4 – AB Cathode

The AB concept was initially developed for electrorefining to:

- Reduce stripping inefficiencies if tankhouses were prone to power outages.
- Improve the life of an ISA 2000 edgestrip.
- Prevent end cap damage.

Power outages alter the initial growth pattern of the copper. When the power is resumed the new growth pattern of the crystals laminates the original copper growth. The resulting lamination can null the effect of the v groove. This can increase stripping times as cathode sheets may require additional movements in the stripping machine to split the enveloped copper. The effect power outages have on the cathodes stripping performance is dependant on the duration, the time in the cycle and the anode overlap. The AB cathode design aimed to reduce the stripping inefficiencies caused by power outages.

In the ISA 2000 cathode plate the bottom corners have square notches of steel removed. The edgestrips have moulded plastic end-plugs, which fit neatly into the voids formed by the notches in the plate. This system eliminates copper nodule growth from the bottom corners. After the early commercialisation of the ISA 2000 technology there were a large number of end cap failures as well as a reduction in the edgestrip life in some refineries. In the standard wax technology the edgestrips do not contact the traverse conveyor and therefore less stress is placed on the edgestrips. The ISA 2000 edgestrips are in direct contact with the traverse conveyor potentially increasing the stresses on the edgestrips. In the AB cathode design the edgestrips do not contact the traverse conveyor.

Experimental Testwork

IPT developed a number of prototypes of the AB cathode based on a 60mm x 60mm chamfer. The results were positive with the corner chamfer reducing stripping inefficiencies when power outages caused lamination of the copper.

At the Townsville Copper Refineries, a cell of 44 AB cathodes were installed and stripped weekly. They were monitored for stripping difficulties, defined by additional movements required by the down ending station to ultimately remove the copper cathode. These additional movements were commonly known as “flaps”. The results from these trials are summarised in Tables 1 and 2.

Table 1 - Stripping data under standard test conditions.
No power outages included.

	No. flaps / 100 strips
AB Cathode	3.3
Standard Cathode	4.2

Table 2 - Stripping data when severe laminations have occurred during the plating cycle.

	No. flaps / 100 strips
AB Cathode	17.3
Standard Cathode	38.5

Under normal operating conditions the standard ISA 2000 cathode plates effectively separated the copper sheets and therefore the improvements were minimal.

The AB cathode improved stripping performance significantly when power outages had laminated the enveloped copper sheets. The additional “flaps” were reduced by half with an AB cathode.

The trials were then extended to include corners of varying shapes and sizes. Smaller corner cut outs as well as rounded corners were trialled. Results indicated that corner chamfers smaller than 40mm x 40 mm and rounded corners performed poorer than a standard v grooved ISA cathode under normal operating conditions. The larger chamfered corners were found to aid stripping performance however were prone to bending over time.

The AB cathode design eliminates the plastic edgestrip contacting the traverse conveyor, reducing fatigue cracking and potentially improving the life cycle of the edgestrips. AB cathodes in service in the Townsville Copper Refinery with an end cap design have been in service for 1.5 years without failure.

As the edgestrips no longer contact the base of the traverse conveyor the v groove is in direct contact with the traverse. Accelerated tests were completed to identify whether any deterioration in the v groove occurred.

An AB plate was lifted and then lowered on to the traverse conveyor a total of 728 times, equivalent to 14 years in service. The impact points on the plate were marked and the measurements were taken from these points through out the test. It was then placed back into service and the plate's performance monitored. Table 3 represents the data collected.

Table 3 - Results from v groove deterioration testing.

No of lowers	Service time	v groove measurements 3 points			Comments
0	0	1.38	1.51	1.52	
208	4 years	1.37	1.37	1.46	slight curling R/H and Mid
312	6 years	1.35	1.32	1.42	slight curling, small chips
468	9 years	1.3	1.29	1.28	curling of contact point edges
728	14 years	1.29	1.34	1.25	no observable change

After the equivalent of 14 years in service the v groove measurements decreased from 1.52 to 1.25 in this area. The tests were undertaken in the ISA PROCESS^{TM} waxless demonstration machine. This machine, unlike production machines does not have a proportional speed control valve to allow the plate to be lowered gently onto the conveyor or soft metal pads for the plate to sit on. The plate descends rapidly onto the steel conveyor therefore making the action far more severe than a production machine. The plate continued to strip successfully after the testwork. This test was completed on several occasions with similar results.

Recently commissioned with the ISA 2000 AB cathode was Sumitomo’s Toyo Refinery in Japan. Approximately 22,000 plates have been manufactured and installed and are reported to be working efficiently. The edgestrip life is also being monitored.

ALTERNATIVE LOWER COST CATHODE PLATE

Current ISA blade material

The standard ISA blade is made of austenitic stainless steel, of grade 316L. It specifically contains 2-3% molybdenum for increased resistance to pitting, and has a low carbon content (0.03%) to minimise chromium carbide precipitation, or sensitisation of welded zones. This decreases the tendency for intergranular corrosion. The typical analysis of 316L is shown in Table 4, [3].

Table 4 – Blade Composition

Element	Composition %
Cr	16-18%
Ni	10-14%
Mo	2.0-3.0%
C	≤ 0.03%
Mn	≤ 2.0%
N	0.04%

The blade is 3.25 mm thick. Based on experience, this is the optimum thickness taking into consideration the plate performance, ease of manufacture and cost-effectiveness. The surface finish is a standard 2B manufacturing finish with a specific surface roughness in the range of 0.25 to 0.6 microns Ra. The high corrosion resistance of the cathode plate is provided by a very thin, tenacious, self repairing layer of chromium oxide, which forms a passive film on the blade, [3].

The development of a lower cost cathode

While the 316L alloy has been the mainstay of the technology since its development in 1978, rising costs and operational considerations in some plants have triggered the ISA PROCESS^{TM} to examine the use of alternative stainless steels in the copper electrorefining (E/R) and electrowinning (E/W) industries.

Increasing costs of metal prices, namely nickel and molybdenum continue to push 316L prices higher and therefore the need for alternative steels suitable for use in the industry was desirable.

The life cycle cost of a cathode was also a consideration in the development of an alternative cathode blade material. The ISA cathodes were developed for a 10-15 year life cycle. Some operations however have a considerably shorter life span and a more economic plate with a life cycle matching the project life would be an advantage. In addition, the extreme operating environments in some plants require plates to be replaced or repaired after 3-4 years.

The focal point of the development work has been on testing a relatively new type of duplex steel, LDX 2101 and the standard 304L stainless steel.

LDX 2101, DUPLEX STAINLESS STEEL

LDX 2101 is a low-alloyed, duplex stainless steel. Its microstructure contains approximately equal amounts of ferrite and austenite. A typical analysis of the duplex steel is Table 5, [4]

Table 5 – Blade composition

Element	Composition %
Cr	21.5%
Ni	1.5%
Mo	0.3%
C	≤ 0.03%
Mn	5%
N	0.22%

LDX 2101 has high mechanical strength due to its duplex microstructure and high nitrogen content. The corrosion resistance is in general at least as good as that of Cr– Ni grades such as 304L and in some cases as good as Cr-Ni-Mo grades such as 316, [4]. The reduction of molybdenum and nickel content reduce the overall price of the steel.

Experimental Testwork

Chemical Resistance Testing

A series of corrosion tests were completed by the Avesta Development Group. LDX 2101, in both a linished and unlinished surface finish was compared against the standard 316L steel and 304L stainless steel. The test parameters are represented in Table 6 and 7.

Table 6 – Test solutions for immersion tests

		Base	1	2	3	4	5	6	7
Cu	g/L	45	45	45	45	45	45	45	45
H_2SO_4	g/L	160	**175**	**195**	**235**	160	160	160	160
Chloride	ppm	40	40	40	40	**55**	**70**	**100**	**120**
Temp	^oC	50	50	50	50	50	50	50	50
Thiorea	ppm	2	2	2	2	2	2	2	2

Table 7 – Test solutions for immersion tests

		8	9	10	11	12	13	14
Cu	g/L	45	45	45	45	45	**15**	45
H_2SO_4	g/L	160	160	160	**175**	**195**	140	195
Chloride	ppm	40	40	40	**70**	**100**	40	100
Temp	^oC	**60**	**68**	**72**	**60**	**70**	50	70
Thiorea	ppm	2	2	2	-	-	-	-
$Fe_2(SO_4)_3$	g/L							**6**

The bold values represent the parameters that were altered from the base line test. The test steels were immersed for 30 days in all tests. Dickson [5] has shown “no uniform corrosion was detected on any of the stainless steel grades in any of the test

solutions. No corrosion rate exceeded 0.01mm/year. No localised attacks, such as pitting or crevice corrosion were observed".

Strength

The LDX is superior in mechanical strength to the 316L stainless steel. The superior strength has allowed plates to be manufactured using a thinner steel sheet. The minimum thickness acceptable is still under investigation. The strength of the steel prevents the manufacturing of plates greater than 3mm thickness. The reduction in thickness, without compromising the strength of the cathode reduces the manufacturing cost of the cathodes.

Flatness Tolerance

The flatness tolerance of commercially available LDX steel is not acceptable for use as cathode plates. Development work in the manufacturing of the steel has allowed the flatness tolerances to fall within acceptable limits.

Surface Finish

The 2B finish has been a successful surface finish for the standard 316L cathode plate. Voids in the surface finish allow the copper to "key" into the steel. This facilitates the adhesion of the copper to the stainless steel in the plating and harvesting cycle, yet permits easy removal once the plate is flexed. Figure 5 is an SEM micrograph showing the 2B surface finish of 316L.

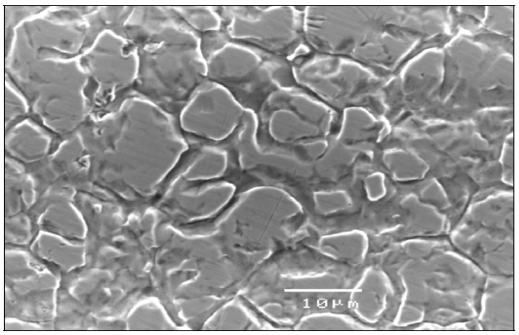

Figure 5 - SEM of 316 L surface magnified 2000x
MacDonald [6]

The nature of the duplex steel does not permit a standard 2B surface finish. A tenacious oxide layer prevents the 2B film from being achieved in the manufacturing process, MacDonald [6].

The achievable mill finishes on the duplex steel do not facilitate the successful adhesion of copper. In tests completed at the Townsville Copper Refineries pre-stripping occurred with a standard duplex mill finish. Figure 6 represents a typical mill finish of the duplex steel.

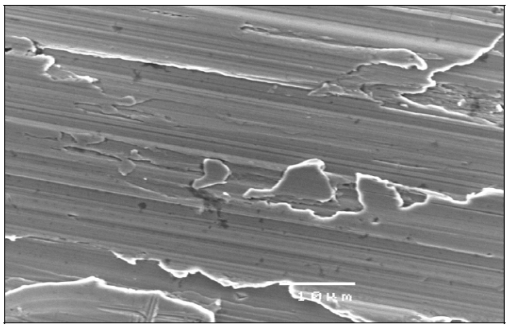

Figure 6 - SEM of LDX 2101 mill finish magnified 2000x MacDonald [6]

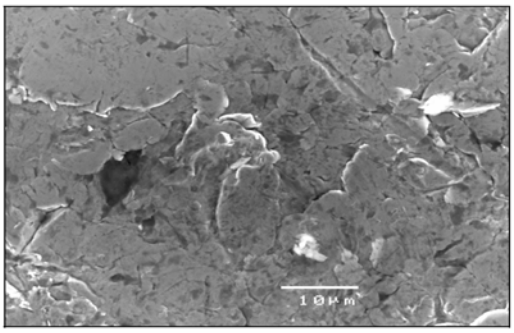

Figure 7 - SEM of LDX 2101 modified surface magnified 2000 x MacDonald [6]

The steels surface has limited voids for the copper to attach itself to. To facilitate the adhesion of copper to the LDX, IPT has developed a unique surface finish for use in the E/R and E/W of copper. An example of this modified surface is presented in Figure 7. Testwork has revealed optimum Ra (surface roughness measurement) values vary for E/R and E/W conditions due to the nature of the copper deposit. The surface finish can therefore be tailored to suit a specific operation.

Operational testing of the LDX 2101 steel

Approximately two cell loads (62 cathodes) of trial plates were manufactured with the LDX 2101 and placed into service at a small electro-winning facility in Australia.

An average analysis of the plants electrolyte conditions are shown in Table 8.

Table 8 – Average analysis of E/W tankhouse

Cu	38-45g/L
H_2SO_4	160-170g/L
Cl	20-30ppm
Mn	90ppm

The cathodes have been in service since the beginning of June 2006 and their physical properties and stripping performance have been monitored. Under standard operating conditions there have been no concerns with the plates.

304 STAINLESS STEEL

The standard 304L stainless steel with a 2B finish was tested in Townsville's Copper Refinery. The plates have been circulating for over 1.5 years with no concerns.

Accelerated corrosion tests were also completed on the steel. Table 6 and 7 represents the immersion tests completed. No uniform corrosion was detected on any of the stainless steel grades in any of the test solutions. No corrosion rate exceeded 0.01mm/year. No localised attacks, such as pitting or crevice corrosion were observed, Dickson [5].

CONCLUSION

Through ongoing development work the ISA PROCESS™ has continued to improve on the original cathode plate design. Past and present testwork still suggests the ISA cathode BR™ is the lowest resistance cathode on the market and the AB cathode has effectively reduced stripping inefficiencies in the ISA 2000 technology. The development of the LDX 2101 as an alternative steel in cathode plates has the potential to reduce capital costs for end users while still providing a technically sound cathode.

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