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PERFORMANCE OF TITANIUM AND NIOBIUM ELECTRODES IN AN
ELECTROLYTIC DISSOLVER FOR NUCLEAR FUELS

R. G. Butzman
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Observations of the performance of materials of construction in the pilot plant dissolver reported here were made by C. A. Zimmerman.

ABSTRACT

Corrosion measurements revealed that titanium could be used, with low corrosion rate, as the cathode-container for an electrolytic dissolver for nuclear fuels operated with 6M or greater nitric acid. The corrosion rate for titanium decreased with increasing nitrate ion concentration at constant current density and increased with increasing current density.

The anodic current-potential characteristics of the valve metals niobium and tantalum were studied in nitric acid. Both the current flow and the corrosion rate, even at 50 volts and 55°C, were low enough to permit the use of either metal as a support for the active platinum anode in the dissolver.

SUMMARY

Corrosion measurements were made to determine whether titanium could be used as a practical cathode construction material for the proposed electrolytic dissolver for nuclear fuels. Concurrent with these experiments, valve metals such as niobium and tantalum were also surveyed to determine whether these metals could be used as insulators to effectively shield the back of the active anode from the cathodic titanium vessel. The corrosion rate of these anodic valve metals was also determined.

These measurements indicated titanium could be used satisfactorily as a construction material for the cathodic container if certain conditions were met regarding the concentration of nitrate ion and current density. Specifically, nitrate ion concentrations of $7M$ or higher effectively passivated titanium from attack at current densities as high as 2 A/cm^2 . Operation with an electrolyte of $6M$ nitrate ion was permissible if the current density was less than 1.0 A/cm^2 .

The current loss or leakage from anodic valve metals such as niobium or tantalum is low (less than 0.1 mA/cm^2) in comparison with the working current dissolving stainless-steel in an electrolytic dissolver. Corrosion rates at dissolvent temperatures less than 55°C are low enough that either of these metals could be considered as insulators to shield the back of the platinum anode from the cathodic vessel.

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PERFORMANCE OF TITANIUM AND NIOBIUM ELECTRODES IN AN ELECTROLYTIC DISSOLVER FOR NUCLEAR FUELS

I. INTRODUCTION

Extensive development work has been done at the Savannah River Laboratory⁽¹⁾ and the Idaho Chemical Processing Plant (ICPP)⁽²⁻⁴⁾ on electrolytic dissolution of stainless steel clad nuclear fuels in nitric acid. Dissolution occurs at a rate proportional to the current density as the stainless steel clad element is made the anode of an electrode couple in nitric acid.

Early experiments at ICPP were made with a metal-to-metal contact dissolver⁽⁵⁾ which used an anode basket to contain the dissolving stainless steel fuel. The perforated basket was fabricated from either niobium or tantalum (electrolytic valve metals). Dissolution occurred as stainless steel was made anodic when placed in the basket^[a].

The presently considered dissolvers utilize the series⁽⁶⁾ or solution-contact principle. These dissolvers consist of an insoluble anode (platinum or platinum-irridium) separated from the cathode by an electrically inert basket. Stainless steel fuel to be dissolved is placed in the basket between the electrodes. As the stainless steel elements intercept current flowing from anode to cathode, part of each steel element becomes anodic and dissolves.

The first horizontal, trough shaped, pilot plant dissolver^(7,8) to be used extensively consisted of a vee shaped trough constructed of titanium metal; one face of the trough served as the cathode for the dissolver. On the other side of the trough, located 0.64 cm from the cathodic surface, a platinum sheet served as the anode. Sheet Teflon was installed in the 0.64 cm space to insulate electrically the back of the anode from the cathode. A schematic cross section of this dissolver is shown in Figure 1.

INC-A-13129

Figure 1 Cross section of the electrolytic dissolver.

[a] These valve metals when placed in an aqueous electrolyte and made anodic, rapidly develop an insulating oxide film. For the dissolution process to occur in the metal contact dissolver, the stainless steel elements must touch and rupture the insulating oxide film and make contact with the underlying anodic metal.

Normally, a cathodic potential is expected to passivate metals from electro-chemical corrosion; however, early work⁽²⁾ at the ICPP indicated significant corrosion occurred as Carpenter-20 was made the cathode of an electrolytic cell in nitric acid. The corrosion rate was dependent on the current density and electrolyte concentration of the cell. In addition, this work also suggested that titanium could be used as a construction material for the cathode of an electrolytic dissolver.

Consequently, the pilot plant trough dissolver was constructed from titanium metal. Results of corrosion observations made on the pilot plant trough dissolver indicated no visible corrosion after 385 hours of operation at varying conditions.

Although plastic or ceramic materials could be used to shield electrically the back of the anode, the preferred construction would be to eliminate both. Preliminary data indicated a valve metal such as niobium or tantalum could provide the necessary shielding. Figure 1 illustrates, in principle, the cross section of the proposed design. Titanium is the proposed material of construction for the cathode-container and niobium is proposed to support and shield the active platinum anode.

The objectives of the experiments reported here were:

(1) To demonstrate the suitability of titanium as a potential cathode, that is to expand the available information regarding the corrosion of titanium as a function of likely processing conditions, and

(2) To determine whether a valve metal such as niobium or tantalum could be used as a practical anode backing material and, if so, would the corrosion rate be low enough for long term use.

The first tentative material balance for the electrolytic dissolution of EBR-II fuel (the first fuel scheduled for reprocessing electrolytically at ICPP) specified a dissolver content and product 3.8M in nitric acid containing 6 g/l uranium. As the corrosion studies reported here proceeded it became clear that cathodic corrosion of titanium was excessive at this concentration, and the nitric acid concentration specified for the material balance was raised to 7.6M with 12 g/l uranium. Corrosion data for both electrodes are given in this document at these and several other acid concentrations.

II. CORROSION OF TITANIUM CATHODE

1. EQUIPMENT AND PROCEDURE

The electrolytic cell used in laboratory studies consisted of a beaker modified so that electrolyte could be continuously recirculated at constant temperature through the cell. The titanium test coupon suspended inside the beaker was faced on both sides by platinum anodes, and the current density on each platinum anode was adjusted so that both sides of the cathode were exposed to equal current densities. Figure 2 illustrates the cell and electrode arrangement.

Tests were made with titanium coupons (ASTM 265 Grade 3) sized 2.5 X 7.6 X 0.48 cm and machined to a 125 RMS surface. Some of these coupons contained a weld area which covered about 40% of the total area of the coupons. These welded coupons were used to determine whether the welded area was preferentially corroded.

Eight different electrolyte compositions (Table 1) were used in these studies, reflecting the search for an electrolyte which gave tolerable corrosion of titanium. In the data tabulated in

Table 1, these are each identified by the total nitrate concentration. The uranium, cations formed from stainless steel, and sodium represented cations which will originate from the dissolution of EBR-II fuel. Boric acid, added in some experiments, represented a soluble neutron poison believed essential for criticality safety in some material balances.

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Figure 2 Cell for determining titanium corrosion.

TABLE 1
ELECTROLYTE COMPOSITIONS

<u>Species</u>									
Total nitrate	M	4.0	6.0	6.2	6.4	7.2	8.0	8.2	10.4
Nitric Acid	M	3.8	3.8	6.0	6.0	7.0	7.6	8.0	10.0
Simulated 304ss	g/l	2.7	30	2.7	5.4	2.7	5.4	2.7	5.4
Uranium	g/l	6.0	66	6.0	12	6.0	12	6.0	12
Sodium	g/l	0.07	0.8	0.07	0.14	0.07	0.14	0.07	0.14
Boric acid	gB/l	---	---	---	2.0	2.0	2.0	---	2.0

The electrolyte solution was prepared by dissolving nitrate salts of the appropriate cations.

2. RESULTS AND DISCUSSION

Variables that were studied and related to the corrosion rate on titanium were (1) welding on test coupon, (2) electrolyte composition, (3) current density, (4) solution turbulence during test, and (5) temperature.

2.1 Current Density and Effect of Welding

Table II illustrates the effect of current density and welding on the corrosion rate of titanium coupons. Each rate measurement was obtained from a single fresh coupon.

TABLE II
CATHODIC CORROSION OF TITANIUM

Electrolyte: 4M nitrate
Temperature: 55°C
Test Duration: 4 hrs

<u>Type of Coupon</u>	<u>Current Density</u> (A/cm ²)	<u>Corrosion Rate</u>	
		mm/yr	(mils per month)
Welded	2.0	21.	(69)
Non-Welded	2.0	18.	(58)
Welded	1.0	10.	(34)
Non-Welded	1.0	9.7	(32)
Welded	0.1	0.06	(0.2)
Non-Welded	0.1	0.09	(0.3)

Data shown in Table II suggested that (1) the corrosion rate varied as the current density varied on the cathode, and (2) that welded and non-welded coupons corroded at essentially the same rate. There was no evidence of localized attack on either the welded or unwelded coupons.

Cathodic current densities from 1 to 2 A/cm² caused no visible or measurable corrosion on the pilot plant trough dissolver; consequently, the data noted in Table II were unexpected in that corrosion rates at 1 and 2 A/cm² would have caused visible and measurable attack on the pilot plant trough dissolver. One significant difference suspected of causing the increased corrosion rate in laboratory tests was the difference in nitrate ion concentration between the pilot plant and laboratory experiments. The pilot plant trough dissolver utilized an electrolyte 7M or higher in nitrate, while initial laboratory tests used the less concentrated electrolyte (4M nitrate).

2.2 Electrolyte Composition

The influence of electrolyte composition was studied by separating the effects of nitrate ion from nitric acid on the corrosion rate in two series of tests.

a. Effect of Total Nitrate on Corrosion Rate

Total nitrate concentration was related to the cathodic corrosion of titanium at two current densities in four-hour tests at 55°C. Results from these tests are shown in Table III.

TABLE III

EFFECT OF NITRATE CONCENTRATION
ON CORROSION RATE

Temperature: 55°C
Test Duration: 4 hrs

Current Density Corrosion Rate, mm/yr (mpm) at total nitrate molarities of:

<u>A/cm²</u>	<u>4.0</u>	<u>6.2</u>	<u>6.4</u>	<u>7.2</u>	<u>8.0</u>	<u>8.2</u>	<u>10.4</u>
1.0	9.7 (32)	1.3 (4.3)	0.73 (2.4)	0.58 (1.9)	---	0.12 (0.4)	0.04 (0.13)
2.0	18	---	---	---	0.91 (3.0)	---	0.46 (1.5)

Increasing the total nitrate concentration obviously significantly reduces the cathodic attack on the titanium coupon.

b. Effect of Nitrate Ion on Corrosion Rate

Although the previous results indicated total nitrate concentration significantly altered the corrosion rate, these results did not indicate whether (a) the hydrogen ion, or (b) the nitrate ion concentration caused the passivation. One test that indicated the nitrate ion concentration was the more significant was made when an electrolyte of 3.8 molar nitric acid was spiked with additional nitrate ion by adding nitrate salts such that the final nitrate concentration was 6M (3.8M in H⁺). This test at 55°C and 1.0 A/cm² gave a corrosion rate of 0.24 mm/year (0.8 mpm). Although not rigorously conclusive, the results strongly suggest that nitrate ion passivated the titanium. The hydrogen ion may also play a role. This result and additional supporting data are shown in Table IV.

TABLE IV

INDEPENDENT EFFECTS OF ACID AND
NITRATE ON CORROSION RATE

<u>Solution Composition</u>		<u>Corrosion Rate</u>	
<u>Nitrate</u> <u>M</u>	<u>Acid</u> <u>M</u>	<u>mm/year</u>	<u>mpm</u>
6.0	3.8	0.24	(0.8)
6.2	6.0	1.31	(4.3)
4.0	3.8	9.7	(32)

2.3 Current Density

In actual plant operation, current densities in excess of 2 A/cm^2 are not likely to be encountered; current densities will be in the range of from 1 to 2 A/cm^2 . Although the effect of current density was previously illustrated in Table I with an electrolyte of 3.8M nitric acid, additional tests were made with electrolytes of higher nitrate concentration at current densities in the range of those likely to be encountered, namely 1.0 to 2.0 A/cm^2 . The results shown in Table III indicate, as did previous data, that operation at lower current densities gives significantly lower corrosion rates.

2.4 Solution Turbulence

In most respects the electrolytic cell used in laboratory tests reproduced conditions projected for the plant dissolver; although, solution turbulence differed significantly. In the laboratory vessel electrolyte flowed at a rate of one volume change of electrolyte per minute to maintain constant temperature of the electrolyte. In the plant dissolver, solution turbulence will result from the inherent design characteristics and operation of the unit. The flow rate through the plant dissolver is projected to be equivalent to 0.3 to 2 solution changes per minute. Since this difference was a potential variable in influencing corrosion rate, the laboratory apparatus was modified to permit a high rate (10 changes per minute) of electrolyte flow across the titanium cathode, to simulate turbulence in the cell. The corrosion rate was doubled at the higher flow rate. With the standard electrolyte at 1.0 A/cm^2 the rate increased from 9 to 18 mm/yr (30 to 60 mpm) as the flow was increased 10 -fold. Tests were not made with an electrolyte of 8M nitrate ion; however, the corrosion rate, if doubled should be less than 0.3 mm/yr (1 mpm) at conditions of high solution turbulence.

2.5 Temperature

In the operation of the pilot plant trough dissolver, temperatures in the dissolver were generally about 50°C; however, occasional temperature variations occurred. To study corrosion at the most common potential operating condition, most laboratory tests were conducted at 55°C. Since temperature upsets occasionally occur, one laboratory test was made at 70°C to determine whether operation at this temperature would significantly increase the corrosion rate. The results observed at both 55 and 70°C gave equivalent corrosion rates at a current density of 2 A/cm².

III. CURRENT FLOW AND CORROSION OF THE VALVE METALS NIOBIUM AND TANTALUM

1. EQUIPMENT AND EXPERIMENTAL PROCEDURE

The cell used to study the current flow (or breakdown potential) and corrosion rate of the two valve metals, niobium and tantalum, consisted of a slotted flask with provision to fit two Teflon electrode holders and electrodes inside with an electrode spacing of 0.635 cm (1/4 inch). Figure 3 illustrates this flask. Electrolyte circulated by a peristaltic pump from a constant temperature bath maintained constant temperature in a given test. A Sorensen "Nobatron" (RC150-7.5) capable of providing dc current at potentials to 150 volts at 7.5 amps served as the power source, while a Sargent strip chart recorder plotted the current flow as a function of time.

Teflon electrode holders held machined electrodes such that only 1 cm² of electrode surface contacted the electrolyte. Electrolyte composition was defined previously in Table I. After the system attained constant temperature, closing the circuit of the power source initiated a given test. The observed current density at constant potential defined the leakage current and steady-state current flow. The weight change of electrodes before and after a given test was used to measure the corrosion rate.

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Figure 3 Cell for determining breakdown of electrolytic valve metals

2. NIOBIUM

2.1 Current Flow

Niobium, when made anodic at potentials of 25 and 50 volts in 4M HNO₃, gave an initial current density in the range of 300 mA/cm². This initial current inflection dropped rapidly, within a few seconds, to current densities less than 10 mA/cm². Progressively, the current density decreased to less than 1.0 mA/cm² after about 5 minutes.

After the current density leveled out, usually at less than 0.5 mA/cm², current surges sometimes occurred. (Fig. 4) These consisted of transient surges of current with a magnitude noticeably greater than the steady-state current density. Usually within one second the current returned to the steady state base line. The magnitude of the surges

in current was more noticeable in tests made at high levels of temperature and potential; however, the peak current density during a given current surge was significantly less than the 300 mA/cm^2 initial inflection.

Figure 4 Current variations for niobium anode at 50 volts and 69°C .
A total of 112 current transients were offscale.

There was no significant difference in the average current density-potential plots for experiments at 38 and 51°C , and at 25, 30, and 50 volts. (Figure 5) The average current density was significantly greater only when the temperature was raised to 69°C at 50 volts.

The characteristic pattern of the current density-time curves plotted on Figure 4 can be explained in terms of an insulating oxide film that forms on the surface of the anode as niobium is anodically oxidized. The rate at which this film forms is proportional to the current density on the anode, but the conductivity through the film, that allows the film to grow, progressively decreases as the film thickness increases. This descriptive mechanism suggests that as electric potential is applied to the clean niobium electrode, current surges sharply through the niobium electrode. This current surge presumably oxidizes niobium to the plus five state, and results in the formation of an insulating oxide film of niobium pentoxide after reaction with either free or nitrate oxygen readily available in the

system. Figure 4 indicates the current density reached a steady-state after 20 to 30 minutes. Niobium pentoxide is an N-type semi-conductor oxide; consequently, a low steady-state current is conducted through the oxide film by a semi-conductor mechanism. This steady-state current likely leads to additional oxidation of the niobium metal, oxidation that occurs at a low rate because of the limited steady-state current density on the anode; but this oxidation, nevertheless, produces additional oxide film. Since the molar volume of niobium pentoxide (calculated as gram atoms of niobium) is greater by a factor of 2.8 than the molar volume of niobium metal, the oxide, once formed, is cramped for space on the surface of the anode. As the oxide is formed on the surface, occasional rupture occurs, and as the oxide is reformed a temporary surge of current passes through the system. These current surges give rise to the current transients displayed on Figure 4. This process of oxidation, rupture, and sloughing of oxide film should result in a net loss of metal which should be detectable by weight loss measurements.

2.2 Corrosion

The results of several 24-hour tests and one 72-hour test aimed at determining the corrosion rate of niobium are shown in Table V.

Table V indicates two methods for determining corrosion rates. First, the current density converted to weight loss yields a corrosion rate based on the steady-state current flowing from the anode, and second, the weight change of niobium (bare metal to bare metal) gives the actual corrosion rate. The results in Table V indicated at temperatures of 50°C or less and potentials to 50V dc, the corrosion was generally acceptable, less than about 0.9 mm/yr (3 mils per month), with fair agreement between rates determined from the steady-state current and weight change data. The only test where the rate was potentially excessive was one test made at 69°C. The rate at this temperature as determined from both current flow and weight change data was undesirably high, in the vicinity of 3 mm/yr (10 mils per month).

All tests were made with a spacing of 0.64 cm, except for one that was made with a spacing of 0.48 cm. As the results shown in Table V indicate, the corrosion rate was acceptable for this test.

Figure 5 Current-density - time relations for niobium

TABLE V
CORROSION OF NIOBIUM ANODE

Electrolyte: <u>4M</u> nitrate							
Potential, dc volts	50	30	50	50	50	50 ^(a)	50 ^(b)
Temperature of Electrolyte, °C	39	50	50	50	69	50	50
Test Duration, hrs	24	24	24	72	24	24	24
Corrosion Rate, mm/year ^(c) from							
steady-state current density	0.50	.43	0.30	0.46	3.41	0.49	----
weight change	0.76	1.00	0.15	0.52	2.71	0.37	0.70

(a) electrode spacing of 0.48 cm

(b) electrolyte: 8M total nitrate

(c) 1 mm/year is equivalent to 3.3 mpm

Two additional experiments were made to determine whether increasing the nitric acid concentration to 8M noticeably influenced the corrosion rate of niobium. These experiments were made because an unacceptable corrosion rate of titanium occurred in an electrolyte of 4M nitrate ion. The experiments indicated changing the nitrate level from 4 to 8M had little effect on the corrosion rate of niobium.

3. TANTALUM

3.1 Current Flow

When tantalum was made anodic in 4M HNO₃, results similar to those obtained with niobium were observed. Like niobium, on closing the circuit, tantalum rapidly formed a protective oxide film that effectively insulated the surface of the electrode from the electrolyte such that little current flowed through the system. The steady-state current density was less than 1.0 mA/cm². The current loss from a working anode backed by tantalum would be negligible in comparison to the current participating in the dissolution of stainless steel.

3.2 Corrosion Rate

As the results shown in Table VI indicate, at temperatures less than 50°C and potentials lower than 50 V dc tantalum corrodes at an acceptable rate for consideration as an anode backing material.

TABLE VI
CORROSION OF TANTALUM ANODE

Electrolyte: 4M nitrate

Voltage, dc	30	50
Temperature of Electrolyte, °C	50	50
Test Duration, Hours	24	24
Corrosion Rate in mm/year (mpm)		
from steady-state current density	0.03(0.09)	0.27(0.82)
from weight change data	0.37(1.1)	0.12(0.36)

Although the electrochemical and corrosion data indicate that either niobium or tantalum would be suitable for the electrolytically inert components of the electrolytic dissolver, the former has been universally selected for pilot plant and plant designs because of its lower density and cost.

IV. RECENT PILOT PLANT STUDIES

Subsequent to the laboratory experimental work reported previously in this report, a pilot plant dissolver 24 inches in length was constructed with a design fundamentally similar to the cross section shown in Figure 1. This pilot plant has been operated approximately 2000 hours at varying process conditions dissolving stainless-steel and portions of EBR-II fuel. At the termination of 2000 hours of testing, the pilot plant dissolver was partially dismantled and examined for corrosive attack.

1. NIOBIUM ANODE SUPPORT

The back of the niobium anode indicated no visible sign of corrosive attack. Slight imperfections were occurring in the vicinity of two of the five ceramic spacers used to support and separate the anode from the cathodic vessel. These wave-like imperfections were shallow and may have been the result of the pressure of the anode resting on the support. Estimates of the corrosion rate after 2000 hours of operation indicated a probable life of at least 1 to 2 years of continuous operation.

2. TITANIUM CATHODE

The only parts of the titanium cathode-container showing visible signs of corrosive attack were those parts of the vessel in a direct line of contact with current from the anode, the areas of the cathode that were likely to have been exposed to the highest cathodic current density. Shaded areas, areas on both ends, and the unexposed cathodic area in back of the niobium supported anode were not attacked. These areas were subject to low cathodic current density.

The side of the vessel facing the platinum anode surface contained numerous small imperfections over the cathodic surface. The surface damage showed a shadow of the wide bands of solid metal in the basket. These imperfections, in most cases, appeared to be small pits up to 2.4 mm in diameter having an estimated depth of about 0.4 to 0.5 mm. Inside most of these pits small particles of bright shiny metal accumulated, metal that was subsequently determined to be stainless steel. Areas in the bottom of the pits were not bright; consequently, these areas were not suspected of being potential anodes with respect to stainless steel.

In the extreme case, with pitting attack proceeding at a rate of 0.17 mm penetration/month, one year of continuous service would yield a penetration of 2.0 mm (0.08 inch). In the active cathode area, the dissolver designed for ICPP will have a wall thickness of 12 to 25 mm, allowing ample corrosion allowance for several years of continuous service.

V. CONCLUSIONS

1. CATHODE

Laboratory results indicate titanium can be used satisfactorily as a construction material for the cathodic container in a full sized electrolytic dissolver if certain conditions are met regarding the concentration of nitrate ion and current density. Specifically, nitrate ion concentrations of $7M$ or higher effectively passivate titanium from attack even when the current density is as high as $2 A/cm^2$. Further, operation with an electrolyte of $6M$ nitrate ion is permissible if the current density is $1.0 A/cm^2$ or less. In general, the corrosion rate is proportional to the cathodic current density. Variables such as solution turbulence, temperature, and hydrogen ion concentration are unimportant as corrosion accelerators at nitrate ion concentrations in excess of $7M$.

Subsequent to concluding laboratory experiments, a pilot sized facility, operated at varying conditions for over 2000 hours, showed only nominal corrosion mainly in areas of high cathodic current density.

2. NIOBIUM ANODE SUPPORT

Laboratory results indicate a valve metal such as niobium or tantalum can be used effectively to insulate the back of the platinum anode from the cathodic titanium vessel. The current loss or leakage from the anodic valve metal to the cathodic container was low in comparison with the working current passing from the platinum side of the anode participating in the dissolution of stainless steel. In addition, corrosion rates determined from laboratory experiments with both niobium and tantalum were low enough at temperatures less than $55^\circ C$ such that both metals could be considered for potential dissolver design. Temperatures of $70^\circ C$ or higher may cause excessive corrosion.

Additional justification for the use of niobium as an anode backing or support metal was obtained in 2000 hours of testing a pilot sized facility. After this extensive operation of the pilot sized dissolver, the niobium backing was not visibly attacked. Since the electrochemical and corrosion performance of niobium and tantalum are effectively the same, the former is preferred because of its lower density and cost.

VI. REFERENCES

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