A Study on the Effect of Crystal Habit Modifiers on the Co-precipitation of REEwith Gypsum

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Abstract Impurity removal is a very important stage of the hydrometallurgical treatment of rare earth elements (REE) processing circuit, which is performed after water leaching of the acid baked REE concentrate. Lime neutralization has a high efficiency in removal of impurities and is the preferred process due to its economic advantage; however, the process has its own problems, such as the production of large volumes of gypsum and co-precipitation of REE with gypsum, i.e. REE loss. This work deals with the effect of several additives (cetryltrimethylammonium bromide (CTAB), polyvinylsulfonic acid (PVS) and polyacrylic acid (PAA)) on the uptake of REE by gypsum from synthesized acidic solutions. The main purpose of this study is to investigate the changes in the crystalline morphology of gypsum precipitated by the addition of crystal habit modifiers and to determine the crystal changes' effects on the uptake of REE by gypsum. In this regard, different concentrations (0.2, 2 and5 g L^{-1}) of above-mentioned additives were studied at room temperature.

Keywords: Rare earth elements (REE) Gypsum PrecipitationCTAB ·PVS ·PAA

Introduction

Acid baking or digestion is one of the favorite industrial processes to digest REE-containing concentrates and ores, which the sands are digested by treatment with an excess amount of concentrated H_2SO_4 at elevated temperatures [1–3]. The resulted pasty material is then treated with cold water to dissolve the REE into solution, leaving the silica, rutile, zircon and undigested concentrate as a residue. After filtering the solution from the gangue minerals, a clear REE sulfate solution is obtained. This solution contains some impurities, such as iron (Fe), aluminum (Al) and thorium (Th) that can create some difficulties for further processing such as solvent extraction as well as additional costs. Therefore, the solution is then treated with a neutralizing agent to remove the impurities from the solution [4].

Lime neutralization has a high efficiency in removal of dissolved heavy metals and the principle of lime neutralization process lies in the insolubility of heavy metals in alkaline conditions. Due to the low lime costs in comparison to other chemicals, it is the preferred process, but has its own problems, such as requiring high dosages of lime to increase the pH and production of gypsum [5]. When the solubility of sulfate and the calcium added from lime exceeds the saturation limit, gypsum starts to precipitate out of the solution [5]. Lime neutralization is the cheapest process for impurity removal stage in hydrometallurgical treatment of REE ores, but is not widely in use due to the fact that a proportion of REE is lost to gypsum, while removing other impurities, such as Fe, Al, Th [4].

Many industrially relevant crystallization processes are influenced by the pres- ence of impurity elements. The negative effects of impurities range from crystal product contamination and alteration of morphology to the formation of other than the intended phase [6].

It is well-known that impurities present in solution may transfer to the crystal- lizing solid. The transfer may take place via interstitial uptake between regular lattice positions, co-precipitation, or isomorphous substitution of one of the ions in the host lattice by the impurity ion or by adsorption [7].

The morphology of dihydrate crystals can be controlled by many methods, one of which is the use of the specific additives. Inorganic and organic crystal habit modifiers have been shown to have an influence on the crystal habit and growth kinetics, but their effectiveness strongly depends on the system, which they are introduced in. They selectively adsorb on the surface of the crystal or nuclei and depending on their concentration, retard or slow down the growth process. They might be effective if there is a good extent of lattice matching between them and the crystal, which means that there should be a good match between the ion spacing of the crystallizing phase and the distances of the functional groups of the additive [8, 9]. The hydroxyl groups of organic additives adsorb on special planes and form hydrogen bond layer, which hinders the touch of growth units with that plane and as a result, the growth would be promoted along other directions [10].

The scope of this study is to develop a novel process to diminish REE co-precipitation with gypsum, while removing the impurities from the solution. Accordingly, a synthesized solution that simulates the leaching solution after acid baking of REE concentrate is used to investigate the effect of morphology changes in the precipitated gypsum crystals by adding $Ca(OH)_2$ on the percentage of REE that co-precipitate with it at low pH values. For this purpose, three crystal habit modifiers, which have been shown [11] to be effective in changing the morphology of calcium sulfate dihydrate precipitates in highly acidic solutions, are used to inspect the changes in the REE uptake by precipitated gypsum.

Experimental

Materials and Reagents

The materials and reagents used in these experiments are presented in Table 1. All chemicals were of analytical grade and de-ionized water was used in all experi- ments. All the experiments were performed in duplicate as a check on the exper- imental technique and precision.

Experiments

Gypsum saturated solution pre-adjusted in pH = 1 by sulfuric acid was first pre- pared and cerium, neodymium, erbium and ytterbium sulfate salts were added to the solution to make a 4 g/l REE-containing gypsum saturated solution. This synthe- sized solution was used as the basic solution for all experiments.

All titration experiments were performed in a Pyrex beaker on a magnetic stirrer (Arex digital, VELP Scientifica) and the pH of the solutions were continuously measured by a pH meter (Fisher Scientific XL600 accumet). The titrant used in these experiments was 5% calcium hydroxide ($Ca(OH)_2$) pulp with the pH value of 13. To investigate the effect of crystal modifiers, three different concentrations of CTAB, PVS and PAA (0.2, 2 and 5 g/L) were added to different solutions at the beginning of the experiments. By adding $Ca(OH)_2$ to the solution, pH was grad- ually changed from 1 to 9 and samples were taken from the solution at the beginning and ending of each experiment (pH 1 and 5). Solutions were filtered in pH 5 and precipitates were collected for characterization. One experiment was conducted with no additive and after filtering the solution at pH 5, the titration was continued to pH 8.5 to determine the complete precipitation of REE in the solution. The crystal morphology of the collected precipitates were analyzed with a FEI FEG-Nova NanoSem scanning electron microscope (SEM) after sputter coating the samples with a thin layer of Cr. X-ray powder diffraction analysis was carried with a Bruker AXS powder diffractometer. Co Ka radiation with a wavelength of 1.79 Å was employed. Chemical analysis was conducted with an Agilent Technologies 4200 MP-AES apparatus. X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Scientific K-Alpha instrument, using an Al Ka X-ray source at 1486.6 eV. Spectra were generated at a

Table 1 Materials and reagents used in this study

Reagent	Grade	Company
Ce(III) sulfate octahydrate	99.9%	Alfa Aesar
Nd(III) sulfate octahydrate	99.9%	Alfa Aesar
Er(III) sulfate octahydrate	99.9%	Alfa Aesar
Yb(III) sulfate octahydrate	99.9%	Alfa Aesar
Hexadecyltrimethylammonium bromide (CTAB)		Sigma
Polyacrylic acid (PAA)	35 wt% in H_2O	Aldrich
Polyvinylsulfonic acid (PVS)	25 wt% in H_2O	Aldrich
Calcium sulfate dihydrate	98%	Acros
Calcium hydroxide		Fisher Scientific
Sulfuric acid	95–98%	Fisher Scientific
Nitric acid	68–70%	BDH
Ce, Nd, Er and Yb standard solutions for MP-AES and ICP	1000 ppm	Alfa Aesar

perpendicular takeoff angle, using a pass energy of 20 eV and steps of 0.1 eV. During analysis, the pressure was in the order of $1.33\,10^{-9}$ Pa. As an internal reference for the absolute binding energies, the Au (4f7/2) peak was used. The experimental spectra were deconvo-luted after subtraction of the Shirley background using the XPSPEAK41 program.

Results and Discussion

The most common way to separate impurities from the sulfate solution is by selective precipitation through controlled acidity. Figure 1 illustrates the titration curve for all four REE used in this study in a regular titration test with no additive. It is clear that around pH 7, REE precipitate out of the solution by increasing pH. But then, in lower pH values, a decrease in the amount of REE ions in the solution is met. This refers to the REE that co-precipitated with gypsum during titration. As it can be seen, the heavy REE are less prone to co-precipitate with gypsum and it can be due to the fact that they have a higher ionic radius difference with Ca^{2+} ions. Therefore, their substitution with Ca ions in the structure of gypsum is more energy consuming than the light ones. Substitution of REE^{3+} ions with Ca^{2+} ions in each plane forms a doped layer in the structure of calcium sulfate dihydrate and the REE cations in the solution are more inclined to substitute the Ca atom on the planes that need less substitution energy.

Table 2 presents the percentage of the four REE investigated in this study in the solution at pH 5. This pH was selected as the target pH at which most of the impurities in the solution, such as Fe, Al and Th have completely precipitated before reaching this pH, meanwhile the REE in the solution have not yet started to precipitate. However, it is obvious that a proportion of REE have precipitated in low pH values, where the impurities are being removed from the solution.

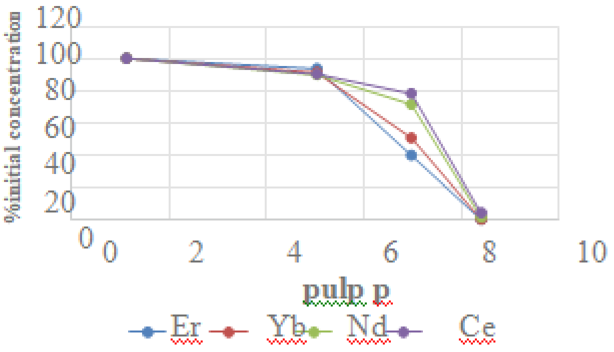

Fig. 1 Titration curve for Er, Yb, Nd and Ce in this study

Table 2 The percentage of Er, Yb, Nd and Ce in the solution at pH 5

Additive	g/L	Er (%)	Yb (%)	Nd (%)	Ce (%)
CTAB	0.2	98.8	97.6	94.8	95.1
	2.0	99.9	99.0	94.7	95.6
	5.0	98.4	97.9	95.1	96.5
PVS	0.2	95.8	95.7	91.5	91.5
	2.0	95.5	94.6	94.8	94.3
	5.0	92.9	91.7	85.4	87.0
PAA	0.2	94.5	93.3	89.2	91.7
	2.0	71.2	64.5	59.7	68.8
	5.0	26.1	20.2	17.4	26.7
No additive	0.0	94.5	93.2	90.7	91.1

Table 2 demonstrates that in the absence of any additive, the solution at pH 5 contains about 94.5, 93.16, 90.7 and 91.13% Er, Yb, Nd and Ce, respectively. This means that about 6% Er, 7% Yb, 10% Nd and 9% Ce have precipitated from pH 1 to 5 and a total of 8% of the REE in the solution are lost to gypsum. This proportion of REE can be either adsorbed on the surface of gypsum or entered the structure of gypsum by substitution with Ca^{2+} ions. The filtrate of this experiment was char- acterized with different characterization methods, which are presented in the following.

Crystal Structure

Figure 2 shows the XRD pattern of the precipitates prepared by $Ca(OH)_2$ 5% titration from pH 1 to 5. It can be seen that the precipitates were composed of calcium sulfate dihydrate (gypsum) phase by the strong peak at 2h =

13.5148°. These were confirmedto be dihydrate and no hemihydrate was detected by XRD, which means that no complete or partial phase transformation occurred in these experiments and gypsum did not go under phase transformation in the presence of REE ions and modifiers (results for the other samples are not provided to avoid repetition).

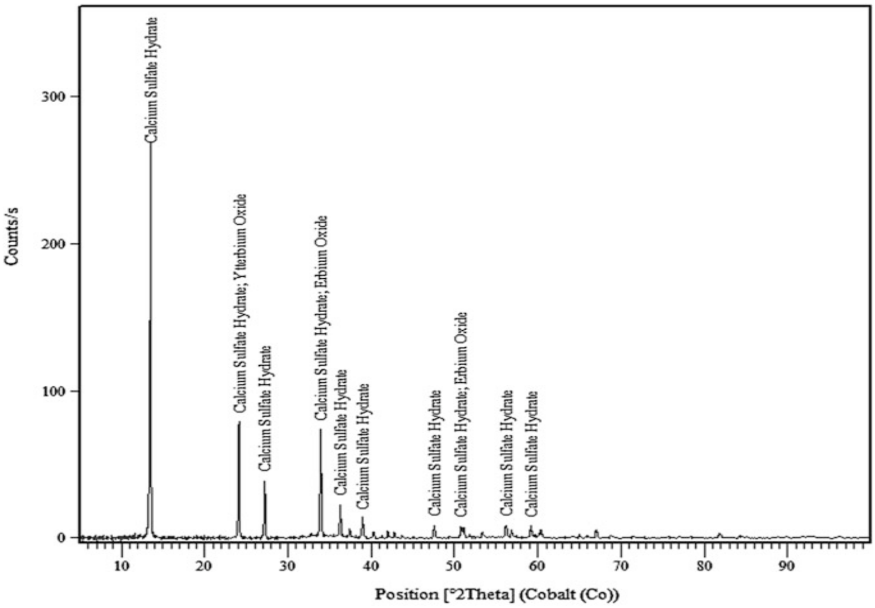

Figure. 2 XRD pattern of the precipitates of titration experiment with 5% $Ca(OH)_2$ at pH value of 5

The XRD results gave no information about the REE species as a result of low concentration of these ions in the structure or amorphous phase formation, except for the heavy ones, erbium oxide and ytterbium oxide that have been detected as minor phases in the structure of gypsum which defines the co-precipitation of heavyREE by means of surface adsorption on specific planes in gypsum crystal structure. This might have happend because of lower tendency of Er and Yb ions to substitute with Ca ions in gypsum crystal structure than the light REE such as Nd and Ce.

X-ray Photoelectron Spectroscopy (XPS)

XPS was carried out to measure the elemental composition of the precipitates. The Shirley method [12] of background removal was used in the least squares fitting. XPS measurements of the binding energy for precipitates are provided in Fig. 3. It shows that Ce, Nd, Er and Yb elements do exist on the surface of the gypsum precipitates. A comparison of the average S2p level binding energy measured by fitting Lorentzian-Gaussian functions to the data gave two peaks with 170.17 and 169.14 eV values. The latter confirmed the presence of $CaSO_4 \cdot 2H_2O$ (binding energy of 169.5 eV) as the calcium sulfate phase which is generated in the course of these experiments as well as the probable presence of $Ce(SO_4)_2$ (binding energy of 169 eV [13]). The former binding energy value

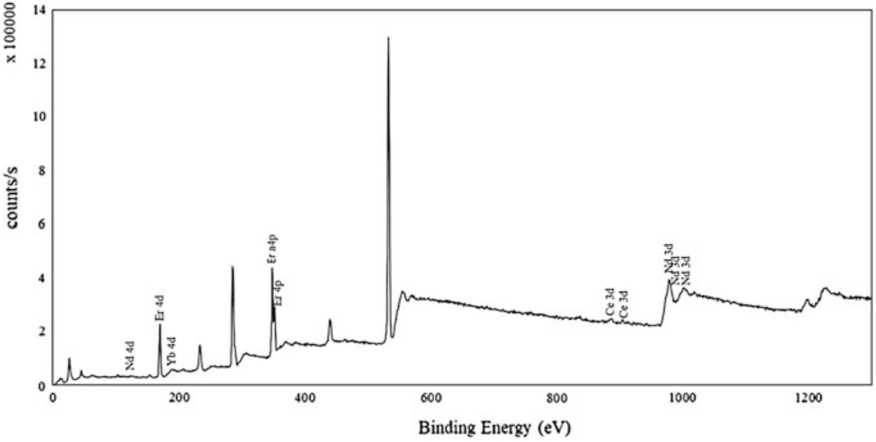

Fig. 3 XPS spectra of the precipitates of titration experiment with 5% $Ca(OH)_2$ at pH value of 5

(170.17 eV) confirms the presence of $Er_2(SO_4)_3$, $Nd_2(SO_4)_3$ and $Yb_2(SO_4)_3$ (binding energy of 170.10 eV) which validates the isomorphous substitution of Ca^{2+} in the host lattice by the REE ions in the solution. Analyzing the peak values for Yb4d, Nd4d, Nd3d, Er4p, Er4d and Ce3d confirmed the presence of $Yb_2(SO_4)_3$ (E_b = 187.30 eV), $Nd_2(SO_4)_3$ (E_b = 122.5 eV), Nd_2O_3 (E_b = 982 eV), Er_2O_3 (E_b = 168.80 eV), CeO_2 (E_b = 907.30 eV) and Ce_2O_3 (E_b = 885.80 eV).

Effect of Modifiers

Table 2 shows the effect of three additives, CTAB, PVS and PAA in three different concentrations on the amount of REE that co-precipitated with gypsum. It is clear from the table that the presence of CTAB in the solution has improved the results; in other words, at pH 5, more REE are present in the solution compared with the regular experiment with no additive. It means that less proportion of REE precipitated with gypsum and REE loss has decreased about 4% for all the REE available in the system. Based on the results, 2 g/L CTAB can be chosen as the optimum condition that is capable of keeping the most percentage of REE in the solution in comparison with the other concentrations of CTAB and other additives. PVS is shown to have a very slight positive effect on the process when it is introduced to the system in 0.2 and 2 g/L, but 5 g/L PVS has shown a negative effect on the process and increases co-precipitation of REE with gypsum. Finally, PAA is shown to have a tremendous negative effect on the process and has increased REE uptake by gypsum.

The different behavior of REE in the presence of the said additives can most likely be due to the different gypsum morphologies, which are obtained when additives are introduced to the system. To investigate the morphology differences in more details, gypsum was precipitated from a REE-free gypsum saturated solution in the presence and absence of the additives. Figure 4 illustrates the morphology of gypsum precipitated from gypsum-saturated solutions in sulfuric acid by changing its pH from 1 to 9 using $Ca(OH)_2$ in the presence and absence of additives. As it is shown, gypsum precipitates in thick elongated plate-shape from the acid solution in the absence of additives and impurities (Fig. 4a). Such plate-like (slab) morphology was also observed in other studies involving the crystallization of calcium sulfate dihydrate in the absence of impurities. Adding CTAB, PVS and PAA to REE-free gypsum-saturated solution caused different gypsum morphologies after precipitation (Fig. 4b–d).

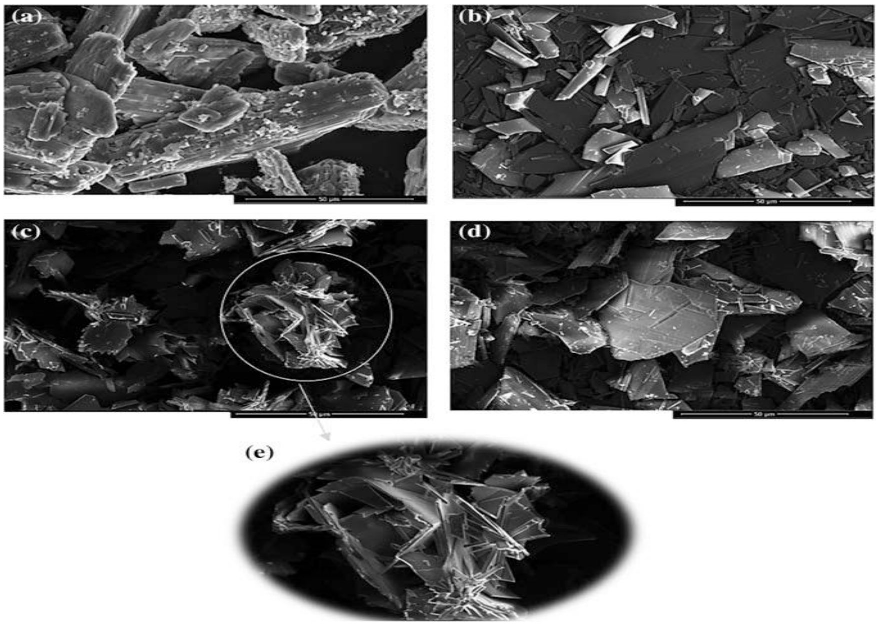

Fig. 4 Morphology of a non-modified, b CTAB, c PVS and d PAA-modified gypsum

An evaluation of SEM images showed that CTAB favored formation of slab (plate-like) crystals but thinner and much smaller than non-modified gypsum (Fig. 4b). CTAB is assumed to act through forming electrostatic ion-pairs between CTAB and surface sulfate groups, namely, preferred adsorption on certain crystal faces that interferes with the crystal growth process [11]. This is the reason of formation of smaller and thinner gypsum crystals in the presence of CTAB in the solution. This suggests that CTAB is probably adsorbed on most of the crystal faces, which are the active sites for REE adsorption on gypsum and results in less REE loss to gypsum while its nucleation and growth process.

Figure 4c represents the morphology of modified gypsum with PVS. As it can be seen, PVS has totally changed the crystal morphology of precipitated gypsum. By comparing Fig. 4c, a we see that very small, elongated crystals have been formed in the presence of PVS in the acidic solution and it is obvious that PVS has strongly retarded growth of dihydrate crystals in almost all directions and some crystals with unknown shapes have been formed. Crystal modification mechanism of PVS is very complex and strongly depends on the crystallization environment. Generally, PVS affects the nucleation and growth process and changes the morphology of the precipitated crystals. PVS can act via two mechanisms; (i) interrupting the periodic incorporation of Ca^{2+} and SO_4^{2-} ions in the structure of gypsum by forming calcium sulfonate complexes instead of calcium sulfate groups which can interfere with the nucleation process or adsorption of the sulfonate groups on the surface of the formed crystals and retarding growth [14]; (ii) the polymeric chain in the structure of PVS may cause steric effects and hence modify the crystal morphology. However, it's been reported by Feldmann and Demopoulos [11] that the steric effect is the main mechanism that PVS modifies the crystal structure of dihydrate crystals in strong acid solutions (in that case HCl) and the detrimental effect seems to originate from the polymeric chain of this additive rather than the sulfonate func- tional group. The dual behavior of PVS in different concentrations is probably due to the complex mechanism of this additive and it might block the preferred adsorption sites for REE on gypsum, but at the same time generate some active adsorption sites by making sulfonate functional groups on the surface of gypsum or the steric effect of the polymeric chain; therefore, the outcome of these two effects can determine the total REE which is adsorbed on gypsum to be more or less than the regular precipitates.

Figure 4d shows the morphology of modified gypsum in the presence of PAA as a surfactant. Compared with dihydrate morphology in the absence of additives, PAA resulted in the formation of thinner and elongated crystals. PAA is postulated to affect the nucleation and growth process by slowing down growth in all faces of the crystal except {011} and $\bar{1}1$f1 .gCarboxylic groups ($-COO^-$) of PAA tend to form polymeric networks in the presence of Ca^{2+} ions; therefore, each Ca^{2+} binds to two PAA ions. This can change the availability of Ca^{2+} ions and subsequently affect the nucleation process as well as the growth process by its preferential adsorption on crystal faces. PAA has a very high affinity towards divalent ions such as Ca^{2+} in any pH value [15]. It forms monodentate complexes with Ca^{2+} even in highly acidic environment that it has a very low dissociation [16]. In addition, the difference between the bond types and energies of $Ca^{2+}–SO_4^{2-}$ ions in dihydrate crystal lattice in the absence and presence of any other ions or additives in the solution that leads to formation of new bonds between ions, can modify the surface energies of specific crystal planes and changes the nucleation and growth kinetics depending on the type of bonds and surface energies. The presumption is that the more PAA available in the system (5 g/L compared to 0.2 g/L), the more Ca^{2+} ions are engaged in binding with the carboxylic groups of PAA and making the network; as a consequence, available REE ions in the system have a higher chance to get into the structure of gypsum and substitute with Ca^{2+} ions. Hence, a high proportion of REE co-precipitate with gypsum before reaching the acidity at which their precipitation occurs.

Conclusion

Selective precipitation of some ions such as Fe, Al and Th from REE-containing leaching solution of acid baked concentrate by means of controlled acidity is a common way to separate these impurities from REE ions in the solution. Application of lime or limestone as a reagent is the cheapest way to change the acidity of solution but has its own disadvantages, one of which is generation of gypsum precipitate and consequently, co-precipitation of a proportion of REE with gypsum. This leads to loss of REE to precipitated gypsum and as a result, lime and limestone have been substituted by much more expensive reagents to avoid the said problem. A novel process was investigated in this paper to decrease the uptake of REE by precipitated gypsum via addition of additives. CTAB additive was shown to improve the REE loss by its preferred adsorption on certain crystal faces that interferes with the crystal growth process. Adding PVS to the system was shown to have a very slight improvement in lower concentrations (0.2 and 2 g/L) and a negative effect in its high concentration (5 g/L). PAA showed a detrimental effect on the process, made a high proportion of REE co-precipitate before the solution reaches the acidity at which their precipitation was supposed to occur. It is pre- sumed to be due to a high engagement of Ca^{2+} ions in making polymeric networks with carboxylic acid groups of PAA that gives the present REE in the solution a higher chance to be involved in the structure of gypsum.

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