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STUDY ON YEN PHU RARE EARTH ORE CONCENTRATE TREATMENT TECHNOLOGY AND SEPARATION OF MAJOR HEAVY RARE EARTH ELEMENTS BY SOLVENT EXTRACTION METHOD

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INTRODUCTION

Yttrium and middle rare earth such as Gd, Eu and Sm of high purity have been used in high-tech fields: function ceramics, phosphors, high temperature superconductor, nuclear materials, [1-3]. Vietnam has various rare earth resources. Yen Phu xenotime contains high concentration of yttrium and middle rare earths. That is why REE ore concentrate from Yen Phu deposit has been chosen to be the research subject on Y and middle REE separation and purification.

In this work, we present research results on separation and purification of some main REE (Y, Gd, Eu and Sm) from Yen Phu REE ore concentrate.

1. The recovery of REE oxides from Yen Phu ore concentrate by alkali decomposition under high pressure

The Yen Phu ore concentrate was decomposed by alkali under high pressure. The decomposition processes were carried out at various quantity of ore concentrate (100 gram and 5.0 kg), and based on these studies, optimum technological parameters such as on ore concentrate/ NaOH ratio, alkali washing, REE leaching by HCl solution and Fe removing by $Na_2S + Na_2HPO_4$ mixture procedures have been determined. The purity of recovered REE solution was more than 99,9% and Fe content was less than 0.09%. This REE solution met the needs of SX separation processes. The composition of REE in the mixture was analyzed and shown in table 1.

Table 1: The composition of recovered REE mixture.

Element	REO(%)
Y_2O_3	26.72
La_2O_3	10.69
CeO_2	12.23
Pr_6O_{11}	5.99
Nd_2O_3	20.64
Sm_2O_3	7.36
Eu_2O_3	0.43
Gd_2O_3	4.86

Tb_4O_7	0.72
Dy_2O_3	4.65
Ho_2O_3	1.06
Er_2O_3	2.37
Tm_2O_3	0.33
Yb_2O_3	1.76
Lu_2O_3	0.20

2- Fractionation of REE oxides into subgroups by SX

The rare earth chlorides were fractionated into three subgroups by SX processes with 1M PC88A in kerosene: LRE (La, Ce, Pr, Nd), middle (Sm, Eu, Gd) and HRE (Dy, Y, ect.). The HRE and middle are further processed to separate the individual REO.

The technological parameters of the fractionation have been optimized using a computer simulation program developed by ITRRE and verified experimentally on mini mixer-settler set. The parameters of fractionation into two subgroups are presented in table 2.

3- Recovery of yttrium concentrate

The HRE chlorides containing Tb_4O_7: 0.01%, Dy_2O_3: 3.1%, Ho_2O_3: 1.6%, Er_2O_3: 8.3%, Tm_2O_3: 1.7% Yb_2O_3: 6.5%, Lu_2O_3: 0.7% và Y_2O_3: 78.0% were subjected to upgrading yttrium concentrate. On the basis of equilibrium data of the SX system Dy^{3+}- PC88A - HCl (table 3) the parameters of the Y concentration process were investigated (table 4) and optimized (table 5) using computer simulation. The enrichment extraction process with these parameters was carried out on the mixer-settler set. The analytical results showed that Gd, Tb and Dy in Y concentrate were eliminated and were in good agreement with simulation program. The composition of the concentrate obtained from the enrichment extraction process could meet the requirements for Y purification by Aliquat 336 extractant.

Table 2. SX parameters for fractionation into subgroups

Feed solution	70 gREO/l; 0.01M HCl
Solvent	1M; 20% neutralized
Scrub. solution	10 gHRE/l; 1.2M HCl
Stripp. solution	3.5 M HCl
Extract. phase ratio	8
Scrub. phase ratio	3,5
Strip. Phase ratio	2
No. of extract. stages	12
No. of scrub. stages	18
No. of strip. stages	12

Table 3: Equilibrium data of the SX system Dy^{3+}- PC88A (1M in kerosene and 5% izodecanol) - HCl at phase ratio O/A = 1 and 20% neutralized by NH_4OH.

Ci = 0.05		Ci = 0.10		Ci = 0.20		Ci = 0.30	
Hi aq	D Dy	Hi aq	D Dy	Hi aq	D Dy	Hi aq	D Dy
0.22	9.290	0.084	3.940	0.083	0.954	0.090	0.490
0.42	2.640	0.168	2.550	0.250	0.654	0.190	0.390
0.630	1.120	0.252	1.720	0.680	0.250	0.380	0.290
1.030	0.315	0.420	0.970	1.010	0.117	0.780	0.130
-	-	0.582	0.575	-	-	1.170	0.050

Table 4. The influence of SX condition on upgrading and recovery yield of yttrium. Feed solution: 20 TREO g/l (Gd_2O_3: 1.5%, Tb_4O_7: 1.4%, Dy_2O_3: 12.1%, Ho_2O_3: 2.4%, Er_2O_3: 6.5%, Tm_2O_3: 0.8% Yb_2O_3: 4.7%, Lu_2O_3: 0.6% và Y_2O_3: 69.8%).

No	O/A in extr.	O/A in Scrub.	Acidity of scrub.	No. of stages		Content of Y and HRE in Y concentrate (%)				Yield of Y+Er %
				Extr.	Scrub.	Er	Y	Ho	Dy+Tb	
						14.2	80.2	2.3	5.2	99
3	2.5	5	1.6	10	10	15.3	82.9	1.6	0.3	99
4	2.5	5	1.7	10	10	15.5	83.2	0.6	0.3	97
5	2.5	5	1.8	10	10	15.6	83.8	0.4	0.3	95
6	2.0	5	1.6	10	10	13.2	83.2	2.5	0.9	99
7	2.2	5	1.6	10	10	14.1	83.0	2.4	0.5	99
8	2.5	5	1.6	15	15	15.3	82.5	1.8	0.4	99
9	2.5	5	1.7	10	10	15.5	83.6	0.6	0.3	99
10	2.5	5	1.7	15	15	15.4	83.9	0.4	0.3	99

Table 5. SX parameters of Y concentrate upgrading process.

Feed solution	20 g REO/L, 0.02M HCl, 14 ml. min^{-1}
Solvent	1M, 20% neutralized; 70 ml. min^{-1}
Scrub. solution	HCl: 1.7M;14 ml. min^{-1}
Strip. solution	HCl: 3.5 M; 35 ml. min^{-1}
Scrub. phase ratio	5
Extr. phase ratio	2.5
Strip. phase solution	2

No. of extr. stages	18
No. of scrub stages	18
No. of strip stages	10

4. Yttrium purification

Some features of the extraction system Y^{3+}/Dy^{3+}- SCN$^-$- Cl$^-$- Aliquat 336 (25% in kerosene)

In order to estimate some features of the extraction system, the influence of NH_4Cl, NH_4SCN and REE concentration on extraction, the distribution coefficients of Y^{3+} and Dy^{3+} (Dy^{3+} take the role of HRE such as Dy^{3+}, Er^{3+}, Ho^{3+}, Yb^{3+} and Lu^{3+}) under various conditions have been determined (table 6).

It was indicated that extraction of Y is considerably less than that of Dy. The distribution coefficients reach high values at concentration of $NH_4SCN >= 1M$. Therefore, 1M NH_4SCN extraction medium was selected for Y purification process.

Modeling of equilibrium data of the system Dy^{3+}-Y^{3+}-SCN$^-$(1M)-Cl$^-$ (2M)-Aliquat 336 (25%)

The equilibrium data of the systems Y^{3+}- SCN$^-$ - Cl$^-$ - Aliquat 336; Dy^{3+}- SCN$^-$ - Cl$^-$ - Aliquat 336 and system containing both Y^{3+} and Dy^{3+} under various extraction conditions have been determined (table 6).

Table 6: Some equilibrium data of the system Dy^{3+} -Y^{3+}- SCN$^-$ - Aliquat 336 (25%)
(20°C, NH_4Cl = 2M, NH_4SCN = 1M)

No	Initial concentration, gram/L		Exp. values gram/L		β	Calc. values, gram/L	
	Y^{3+}	Dy^{3+}	$[Y^{3+}]$aq.	$[Dy^{3+}]$aq.		$[Y^{3+}]$aq.	$[Dy^{3+}]$aq.
1	5	3	3.5	0.8	5.8	3.0	0.2
2	7	3	4.9	0.9	5.2	4.7	0.4
3	9	3	6.7	1.1	5.2	6.5	0.6
4	15	3	11.7	1.3	4.9	12.2	1.2
5	20	3	15.8	1.4	4.2	16.1	1.7
6	5	5	2.4	1.7	4.9	3.3	1.3
7	20	5	16.1	2.3	4.7	16.4	2.7

The data showed that the distribution coefficient of REE ions or total equilibrium concentration of REE ions in the aqueous phase of the SX system: Aliquat 336 (25% in kerosene) - RE_1^{3+} - RE_2^{3+} - NH_4Cl - NH_4NCS depends on concentrations of NH_4Cl, NH_4 NCS and REE ions. This dependence is complicated and there have been no mathematical models for this system. In this work, artificial neural networks, in particular, the neural networks of back - propagation of errors has been used for modeling the system [5-7]. These neural networks took the role of two functions, which described the equilibrium data of the SX systems:

$$[Y^{3+}]aq = f(Ci\ (Y),\ Ci(Dy)) \quad \text{and} \quad [Dy^{3+}]aq = f(Ci\ (Y),\ Ci\ (Dy))$$

Where: $[Y^{3+}]aq$, $[Dy^{3+}]aq$ are equilibrium concentrations of Y^{3+} and Dy^{3+} in aqueous phase; Ci(Y) and Ci(Dy) are initial concentrations of Y^{3+} và Dy^{3+} in aqueous phase, respectively.

The experimental verification of the neural networks showed that calculation and experimental values are in good agreement.

A computer simulation program has been developed based on data modeling and principles of the counter-current SX process. Optimized SX parameters of the Y purification has been found by using the program (Fig. 2).
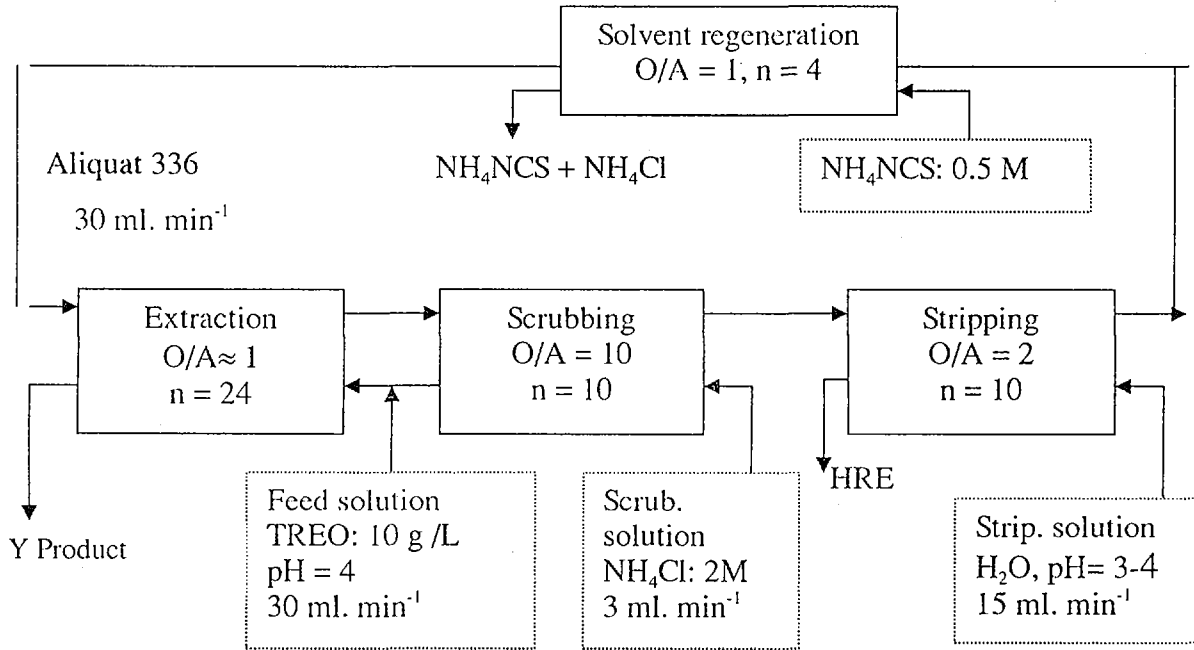

Fig. 2. Flowsheet for Y_2O_3 purification using Aliquat 336 in SCN^- - Cl^- medium.

The experiment was carried out on mixer-settler set and it was shown that the yield of the process was more than 85%. The purity of the obtained Y_2O_3 was 99.9%.

5. Isolation and purification of Eu

The middle subgroup separated from Yen Phu REE oxides containing 3.7% Nd_2O_3, 3.2% Eu_2O_3, 57.2% Sm_2O_3 and 35.6% Gd_2O_3 was subjected to isolation and purification of Eu. The Eu recovery consisted of several steps: the Eu concentrate recovery; the first purification by reduction on Zn column and the $EuSO_4$ precipitation and the second purification by reduction and precipitation out of RE^{3+} ions in the form of $RE(OH)_3$ at the pH of 10 (buffer NH_4Cl - NH_4OH).

The technical parameters for each steps have been established: the contact time for reduction on Zn column was 10 min.; pH of the feed solution for reduction was found to be 2.5-3.0; the precipitation agent Eu^{2+} was H_2SO_4 with the ratios between H_2SO_4 and Eu of 3-5. The reduction and Eu precipitation in the form of $EuSO_4$ should be carried in CO_2 atmosphere. The second purification should be carried in N_2 atmosphere and at the pH of buffer of 10.

Under the above conditions, the purity of recovered Eu was found to be 99.9% and overall yield was more than 80%.

6. Separation and purification of Gd

The middle subgroup obtanied from Eu isolation containing 4.0% Nd_2O_3, 0.2% Eu_2O_3, 59.1% Sm_2O_3 và 36.6% Gd_2O_3 was subjected to separation and purification of Gd by SX technique with PC88A extractant. The SX parameters were optimized using simulation program and experimentally verified (table 7).

Table 7. SX parameter for Gd separation.

Feed solution	33 g/l, HCl: 0.05M, 7,5 ml. min^{-1}
Solvent	1M, 20% neutralized; 30 ml. min^{-1}
Scrub. solution	HCl: 1.0M, 2 g Gd_2O_2/l; 6 ml. min^{-1}
Strip. solution	HCl: 3.5 M; 15 ml. min^{-1}
Scrub. phase ratio	5
Extr. phase ratio	2,5
Strip. phase solution	2
No. of extr. stages	12
No. of scrub stages	12
No. of strip stages	6

Under the condition with these parameters, about 100 gram Gd_2O_3 of 98% has been recovered. The yield of the process has been determined to be about 90%. Besides Gd, Sm concentrate (concentration of Sm_2O_3 is about > 85%) was separated. The main impurity in the Gd_2O_3 was Eu, which was separated from Gd by the reduction and then precipitated with H_2SO_4 giving the purity value of Gd_2O_3 of more than 99%.

7. Overall schema for recovery of some REE oxides from Yen Phu ore concentrate

Based on the above-obtained results, an overall scheme for recovery of some REE oxides from Yen Phu ore concentrate using SX and oxidation-reduction techniques has been proposed (fig. 2).
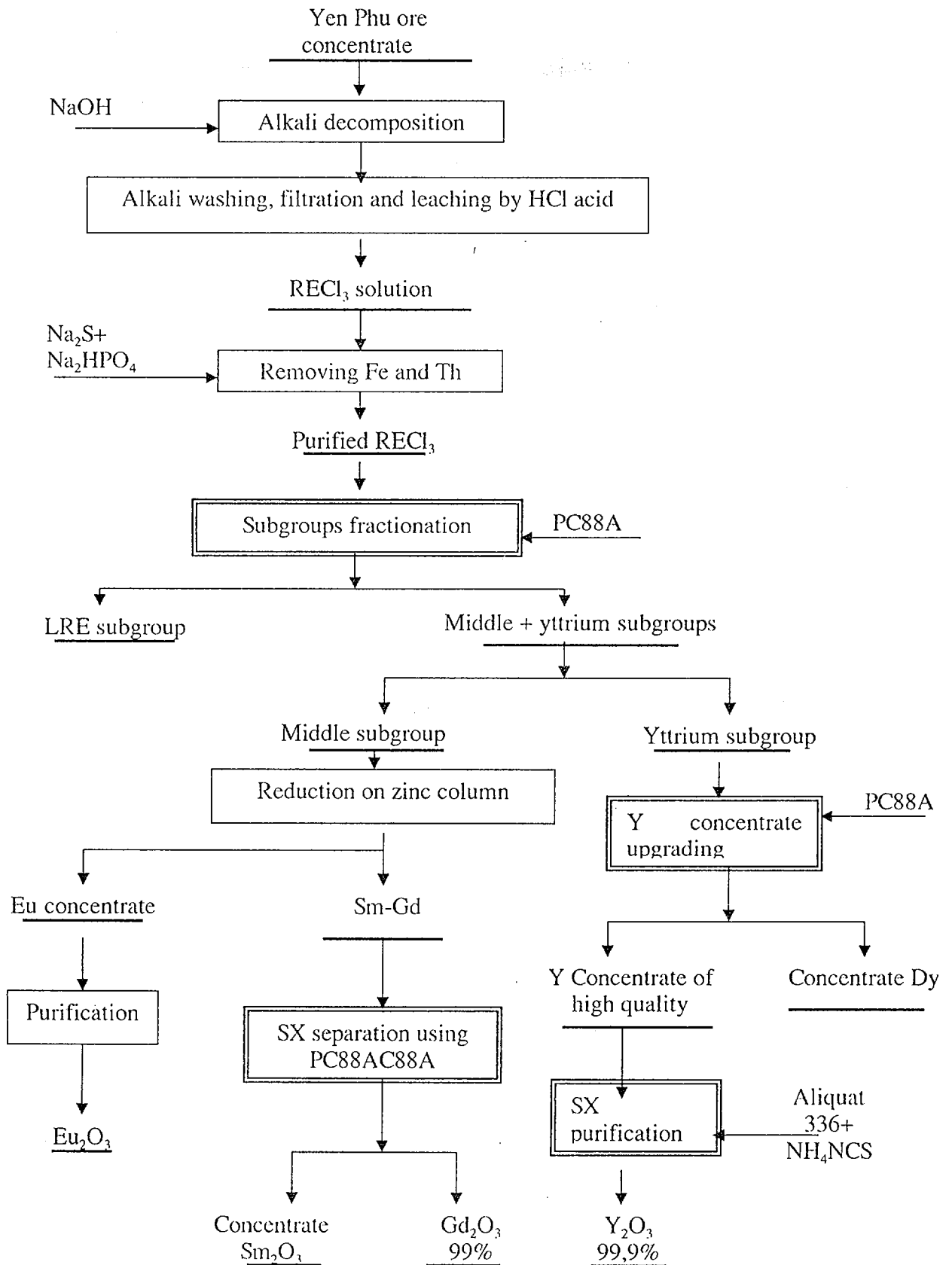
Fig.1. Overall scheme for recovery of some REE oxides of high purity from Yen Phu ore concentrate

CONCLUSIONS

1. The decomposition of Yen Phu REE pre-concentrate, leaching and removal of impurities have been carried out. The impurities in recovered oxides satisfied SX separation process requirements.

2. The flowsheet for fractional extraction into subgroups using PC88A extractant has been established.

3. The optimum parameters for upgrading Y concentrate using PC88A have been determined.

4. The modeling of equilibrium data of SX system containing Aliquat 336, Dy and Y in NCS^--Cl^- medium and the simulation of SX separation process of Dy-Y using Aliquat 336 extractant have been carried out. Based on these studies, the optimum parameters for purification of Y_2O_3 99.9% have been found out. And Y_2O_3 was recovered from high quality concentrate of Y.

5. The conditions of isolation of Eu by reduction on Zn column and the precipitation in the form of $EuSO_4$ in combination with the purification of Eu by reduction and Eu precipitation from RE^{3+} ions with ammoniac buffer (pH = 10) have been determined. The purity of recovered Eu_2O_3 is > 99.9%. Eu^{3+} has been reduced on Zn column then precipitated from RE^{3+} solution in the form of $EuSO_4$ followed by the further precipitation with ammoniac buffer (pH = 10) in order to be seperated and purified from RE^{3+} ions, giving the product of more than 99% Eu_2O_3.

6. The flowsheet for Gd separation and purification of Gd of 99% purity has been developed.

7. The overall schema for Yen Phu REE ore concentrate treatment and individual recovery has been proposed.

8. The obtained results are necessary steps for scaling up bulk recovery of individual REE from Yen Phu ore concentrate containing high concentration of heavy and middle elements.

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THE PREPARATION FOR RARE EARTH MICROFERTILIZER AND THEIR APPLICATION FOR INCREASING THE CROP YIELD OF TEA TREES

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INTRODUCTION

It has been known that Rare Earth Elements widely exist in the earth crust at the average content of 0.0153 % R_2O_3. The content of Rare Earth Elements in the soil is in the range of 0.015-0.02 % R_2O_3. Rare Earth Element content in plants and in the lake-water have been found to be approximately 0.003% and < 0.001 ppm R_2O_3, respectively. Thus, it seems that plants absorb rare earth elements from the soil for their growing up. Based on the practice of tea plantation, it could be realized the crop yield of tea in Tam Duong, Phong Tho, Lai Chau was higher than in many other areas in North Vietnam and the quality of tea products in those areas was also better. It was noticed that Tam Duong tea farm is located very closely to a rare earth mine in Phong Tho. Therefore, a question that whether rare earth elements have a good influence on the crop yield of tea has been taken into consideration.

The study on the application of microfertilizers containing very low contents of Rare Earth Elements to about 50 kinds of crop plants have been conducted in China, Australia ... The experimental data showed that the use of rare earth microfertilizers could give much higher crop yield and better quality of the products. (see table 1)

Table 1. The influence of Rare Earth on the crop yield of various plants

Crop	Increment of crop yield (%)	Crop	Increment of crop yield (%)
Apple	10-15	Cucumber	8-15
Rice	5-10	Sugar-cane	10-15
Grape	8-12	Rubber- tree	8-14
Corn	6-11	Cabbage	10-20
Cotton	7-10	Wheat	6-12
Soy-bean	5-10	Tea	8-12
Tomato	10-15	Sugar-beet	6-12
Banana	8-15	Water-melon	8-10
Orange	5-10	Peanut	8-12
Pepper	8-15	Longan	10-20
Tobacco	10		

EXPERIMENTAL

During the past two years (2001-2002), under the frame work of the Ministry Project *"Study on the preparation for some Rare earth products for increasing tea crop yield"*, some experiments have been carried out to produce several kinds of rare earth microfertilizers in the forms of soluble salts for leaf spraying and slowly-soluble salts mixed with carrier reagents which are able to adsorb and accumulate dissolved rare earths before supplying for plants for soil fertilizing. A technological process has been found for preparing two kinds of rare earth microfertilizers as follows:

- DH 1 for leaf spraying is a light-yellow fine suspensoid solution which contains 10% rare earths.

- PBD1 for soil fertilizing is a powder mixture of rare earth microfertilizers with macro fertilizers N, P, K at the ratio of 2:3:3:4 in which rare earth microfertilizer contains 85% carrier reagents and 15% rare earths. These kinds of microfertilizers have been first experimentally applied to tea-trees in some places in the North of Vietnam such as Song Lo Tea Company (Tuyen Quang province) and Cuu Long Farm (Hoa Binh province).

During the experiments, the available beds of tea which have the same area and growth were chosen. The control beds were also fertilized and watered (using water without rare earths) in the same way as the experimental beds (sprayed and soil manured with various doses of rare earths). The skilled and experienced workers have also been chosen for collecting tea leaves so that we could obtain good experimental data.

The experimental data showed that the application of 300kg/ha of PBD1 Rare earth micronutrient (a mixture of NPK with a very low amount of rare earths), exhibited a significant increase in fresh tea crop yield (10 - 30 %) compared to the controls (without the treatment with PBD1 Rare earth microfertilizer). When DH 1 was used for leaf spraying, fresh tea crop yield increased from 20.5 to 38.6 % compared to the controls with the increase of A quality product of 33%. Furthermore, the application of the Rare earth microfertilizers to soil treatment and leaf spraying seemed not to cause any bad effects on the quality of tea products: no strange smells and tastes could be sensed, even though in some samples, better flavours and tastes could be perceptibly realized in comparison with the controls (see Tables 2 and 3).

Table 2. The influence of REE solid microfertilizers PBD1 on the dry matter yield of tea in the Song Lo Tea Farm, Tuyen quang province.

Plot of land	REE amount (kg/ 360m^2)	Dry matter yield of tea (kg)					Crop yield increase (%)
		Haverst. time 1	Haverst. time 2	Haverst. time 3	Haverst. time 4	Average yield	
Control D 0-1	7 NPK + 0 REE	-	10.2	9.6	14.7	11.5	0
D1	7 NPK + 0.5 REE	-	10.0	9.0	17.5	11.2	-2.6
D2	7 NPK + 1.0 REE	-	10.0	10.5	16.7	12.4	+7.8
D3	7 NPK + 1.5 REE	-	11.3	11.2	15.7	12.7	+10.4
D4	7 NPK + 2.0 REE	-	10.8	13.4	15.5	13.2	+14.8

EXPERIMENTAL CONDITIONS

- REE concentration in the initial solution of REE liquid microfertilizers ĐH1 was 50gREE/l.

- The solution of REE liquid microfertilizer ĐH1 was diluted in 20 liters of water before used for tea leaf spraying in all the plots of land.

- In the plot P5, an amount of 1000g tender tea leaves was picked after each period of time of 1, 3, 5, and 10 days for the determination of REE contents in tender tea leaves.

Plot of land	REE amount (kg/sao), 1sao = 360 m^2	Dry matter yield of tea (kg)					Crop yield increase (%)
		Haverst. time 1	Haverst. time 2	Haverst. time 3	Haverst. time 4	Average yield	
Control P0	0	-	3.6	9.4	13.5	8.8	0
P1	125	-	7.2	11.1	15.0	11.1	26.1
P2	250	-	6.8	11.6	16.5	11.6	31.8
P3	375	-	6.3	9.9	17.5	11.2	27.3
P4	500	-	7.9	9.4	19.4	12.2	38.6
P5	625	-	6.0	9.1	16.7	10.6	20.5

It could be generally seen that tea trees in the experimental plots of land seemed to be higher with larger vaults of obviously darker green colour tea leaves than those in the controls. Especially, the tea trees in the experimental plots of land did not have to suffer from any garden pets or diseases while we could notice the bad effects of pets scattering in the control plots and they needed to be sprayed several times with perticides.

Apart from these, some preliminary experimental studies on the effects of dissolved rare earth contents available in the soil on the increase of tea crop yield have also conducted. It seemed that the increase of tea crop yield in the plots of low easily-dissolved rare earth salt contents was significantly bigger than in the plots of high easily-dissolved rare earth salt contents. Analytical data also pointed out that no significant differences in rare earth contents in tea products with and without treated with RE microfertilizers could be found.

CONCLUSION

Application of RE microfertilizers not only gives better crop yield and quality of tea products but it also strengthen the resistibility/resistance to pets and diseases of tea trees. As a result, the use of perticides/insecticides can be considerably reduced. Analytical data also showed so small remaining contents of RE in tender tea leaves that we can believe in the safety of tea products. Based on the published studies on the effects of rare earths on physiology and crop yield for a number of economically important agricultural plant species, some conclusions could be drawn as follows:

- Under proper conditions, the RE nutrients could considerably promote crop yield without causing bad effects on the product quality. The photosynthesis of plants

have been found to be enhanced by 20-80% by application of REE, giving a potential increase in yield and dry matter production for a number of agricultural plants at rather low cost.

- Application of REE microfertilizers also enhances the metabolism process of plants and prevent the loss of NPK macrofertilizers in the soil, reducing the cost of fertilizing but without changing the contents of important minerals in plant tissues such as N, P, K, S, Ca, Mg, Na, Mn, Fe, Cu, Zn, B and Cl, which are vitally needed for the growing up of plants.

- Application of rare earth microfertilizers can cause enhanced rates of development of plants, especially plant rooting, germinating and vitality, resulting in their better ability to withstand low soil moisture or drought and better resistance to infection.

- When low rates of rare earth microfertilizers were used, no considerable indication of toxicity was observed in experimental plants compared to the controls.

- However, the application of too large RE doses (>1,000g La/ha, for example), the crop yield seemed to be less increased and even reduced because of the RE poisoning of the plants, but residual contents of RE accumulated in plants were found to be higher. Thus, proper doses, time and frequency must be carefully selected for the RE utilization in plants in order to ensure that it cannot do any harm to plants, living creatures and the environment as well.

In order to confirm the effects of rare earth microfertilizers application on tea production and crop yield as well as the quality and safety of tea products, further studies and experiments should be conducted on larger scale, longer periods of time. Physiological studies on the influence of rare earth microfertilizers on plant development should also be performed together with the confirmation of the safety of tea products.

It is hoped that the preliminary results of this project will be more widely applied in our agriculture, so that they can partly contribute to the poverty-alleviation movement in the midland and mountainous regions, and effectively exploit rare earth resources in Vietnam.

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