S. MASTROLITTI

Energy Technologies Department – Bioenergy
Biorefinery and Green Chemistry Division
Bari territorial office

M. MORGANA, G. DE VINCENZIS

Energy Technologies Department – Bioenergy
Biorefinery and Green Chemistry Division
Research Center, Rotondella (Matera)

G. DI SANZO

Territorial and Production Systems Sustainability
Department – Biotechnologies and agroindustry Division
Research Center, Rotondella (Matera)

F. BALDASSARRE

CNR – National Research Council of Italy
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NOVEL RARE EARTHS EXTRACTION PROCESS BY SUPERCRITICAL CO_2 AND TBP-HNO_3 COMPLEX (PRELIMINARY EXPERIMENTS)

The Treibacher Industries-ENEA experience

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ITALIAN NATIONAL AGENCY FOR NEW TECHNOLOGIES,
ENERGY AND SUSTAINABLE ECONOMIC DEVELOPMENT

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S. Mastrolitti, M. Morgana, G. De Vincenzis, G. Di Sanzo, F. Baldassarre

Abstract

The scientific collaboration between ENEA and Treibacher Industry AG (TIAG) had the aim to develop a novel hydrometallurgical extraction process for the recovery of rare earths, and Yttrium in particular, from waste or other new alternative raw material sources. Research activities were carried out by the two groups using facilities, available laboratories and sharing know-how and skills.

Within this cooperation, between 2013 and 2015, ENEA fitted its mission on sustainable development and environmental safety, and TIAG reached an efficient extraction and purification process. Among the tested extraction methods was employed also a bench scale plant, working with supercritical fluids, usually busy for the extraction of natural essences and oils.

Supercritical CO_2 technique (CO_2-SC) is nowadays mostly used to extract organic compounds from vegetal matrices. Recently it has found, in metal extraction, a new application field. CO_2-SC assisted metal extractions, usually needs a ligand among which the Ter-n-butyl phosphate (TBP) is one of the most employed. For these applications, among the TBP-based ligands, the ones obtained combining TBP and nitric acid, having the non-specific formula $TBP(HNO_3)x(H_2O)y$, often are reported in literature [1-31].

These ligands were studied in this work on a simple matrix containing a mix of La_2O_3, Nd_2O_3, Eu_2O_3, and Y_2O_3 (granulometry ≤ 40 µm) in order to reach the best working condition for the extraction, separation and purification of every rare earth.

Among the rare earths these four (La, Nd, Eu, Y) are often present, either in mining rocks, or in WEEEs, are among the more precious, and cover almost all the different chemical-physical properties of the rare earths. Thus they were chosen with the aim of create a simple but representative matrix.

The CO_2-SC technique was also tested on a waste powder obtained from lamps and delivered by TIAG.

Key words: Supercritical CO_2, Rare earths, metal extraction

Riassunto

La collaborazione scientifica fra ENEA e Treibacher Industry AG (TIAG) è basata sulla ricerca e ottimizzazione di un processo idro-metallurgico atto ad estrarre e purificare terre rare (in particolare Ittrio) da rifiuti e altri materiali grezzi. Questa ricerca incontra anche gli interessi ENEA in merito alla salvaguardia ambientale e alla sostenibilità.

Al fine di traguardare questi comuni interessi, è stato stilato un accordo che ha coronato la proficua collaborazione e lo scambio di conoscenze di due team di ricerca (uno di ENEA e l'altro di TIAG) con le relative apparecchiature nel triennio 2013-2015. Uno dei temi di ricerca ruotava attorno all'uso di fluidi supercritici e complessanti per estrarre e purificare terre rare da varie matrici.

L'Anidride Carbonica (CO_2) in condizioni supercritiche, finora ampiamente utilizzata per estrarre e concentrare composti organici da matrici vegetali, recentemente ha trovato un nuovo campo di applicazione nell'estrazione dei metalli. Quest'applicazione in genere necessita di un complessante e fra i complessanti più utilizzati figura il Ter-n-butyl phosphate (TBP). In particolare combinando TBP con l'acido nitrico e l'acqua si possono creare diverse tipologie di complessanti la cui formula bruta si può riassumere nella formula generica $TBP(HNO_3)x(H_2O)y$ spesso riportata in letteratura [1-31].

In questo lavoro è stato utilizzato di uno dei complessanti appartenenti a questa famiglia su una matrice semplificata di ossidi di terre rare contenente La_2O_3, Nd_2O_3, Eu_2O_3, and Y_2O_3 con lo scopo di iniziare un'indagine tesa a valutare le migliori condizioni di lavoro per incrementare sia le rese di estrazione che la separazione e la purezza delle terre rare estratte. In particolare l'ottimizzazione ricercata in questo lavoro si riferisce, sia ai tempi di contatto fra la matrice semplificata e il sistema estraente costituito da CO_2 supercritica e complessante, che alla quantità di matrice sottoposta al processo di estrazione. La scelta della matrice semplificata (solo 4 terre rare) è legata alla necessità (in questa fase iniziale della ricerca) di limitare le variabili in gioco. La scelta proprio delle 4 terre rare La, Nd, Eu, Y è legata alla necessità di Treibacher di mettere a punto un efficiente sistema di estrazione e purificazione di Y a partire da matrici complesse contenenti le 4 terre rare indicate. La suddetta matrice semplificata suggerita da Treibacher incontra anche le esigenze di ricerca dell'ENEA in quanto questa matrice mima, non solo la composizione di alcune rocce minerarie provenienti da giacimenti di terre rare, ma anche la composizione di alcuni RAEE, e quindi, l'approfondimento delle conoscenze relative alla estrazione, separazione e purificazione delle terre rare di questa matrice semplificata, può trovare applicazione in ambito industriale favorendo la salvaguardia ambientale e lo sviluppo sostenibile.

Infine è bene sottolineare che le 4 terre rare scelte, avendo proprietà chimico-fisiche fra loro differenti, costituiscono una matrice semplificata da cui si potrebbero teorizzare applicazioni su modelli più complessi.

Nell'ambito di questa ricerca sono anche state testate le potenzialità di questo approccio di estrazione e purificazione anche su una polvere ottenuta da lampade esauste conferita da TIAG.

Parole chiave: Fluidi supercritici, Terre rare, estrazione di metalli

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1. Introduction

Supercritical CO2 technique (CO2-SC), till now widely used to extract organic compounds from vegetal matrices, recently has found, in metal extraction, a new application field. CO2-SC assisted metal extractions usually needs a ligand among which the Ter-n-butyl phosphate (TBP) is one of the most employed. The combination of TBP with Nitric acid and water develops a wide family of ligands, having the non-specific formula TBP(HNO3)x(H2O)y, often reported in literature [1-31]. These ligands (TBP-HNO3) were studied, in this work, on a simple matrix containing a MIX of La_2O_3, Nd_2O_3, Eu_2O_3, and Y_2O_3 (granulometry ≤ 40 μm) in order to reach the best working condition for the extraction, separation and purification of every rare earth. Among the rare earths these four (La, Nd, Eu, Y) are often present, either in mining rocks, or in WEEEs, are among the more precious, and cover almost all the different chemical-physical properties of the rare earths offering a simple but representative matrix. Moreover it was chosen this rare earths group (La, Nd, Eu, Y) because, it fits, either the necessity to work with a simple system, or the TIAG interest in Y extraction and purification. The tests have been performed by means of a bench scale CO2-SC plant usually used for the extraction of natural oils and essences from agricultural matrices. This unusual use of this kind of bench scale plant for the Rare Earths (RE) extraction is widely reported [11, 19, 22].

Among the starting up activities were optimized the procedures for:

1) preparation of TBP-HNO3 complex to be used for the extractions;

2) extraction without CO2-SC at room temperature;

3) samples collection from the plant after the CO2-SC assisted extraction;

4) storage till the analytical steps;

5) retro-extraction of the stored samples into an aqueous phase ready for the analytical steps;

6) analysis by ICP-OES.

The optimized procedures were than applied and were collected a lot of data discussed in the last paragraphs.

1.1 Acronyms

CO2-SC	Supercritical carbon dioxide
WEEE	Waste of Electric and Electronic Equipment
RE	Rare Earths
MIX-1	RE Oxides MIX - (W% $\Rightarrow$ Y_2O_3 18,60 - Eu_2O_3 25,77 - Nd_2O_3 18,83 - La_2O_3 20,03)
MIX-2	RE Oxides MIX - (W% $\Rightarrow$ Y_2O_3 23.65 - Eu_2O_3 22.67 - Nd_2O_3 18.31 - La_2O_3 23.13)
TBP	Ter-n-Butyl Phosphate
EXC	Static extraction conditions - (Temp.=50 °C, Press.=150 bar, time=1h)

2. Materials and methods

2.1 CO2-SC plant: main characteristics, procedure and settings for the extraction

The plant used for the tests is shown in figure 1.

In the upper part there is the oven which contains 2 identical steel vessels (cylindrical, internal diameter ~ 2 cm, volume 32 ml) connected with a steel tube. The one on the left has a preheating function for the CO_2-SC, in the other one is performed the extraction (the CO_2-SC income from the lower part of the vessel). The oven is equipped with a thermocouple which checks the reaction/extraction vessel temperature.

In the lower part, there is the control desk by which the CO_2 pressure and the contact time between CO_2-SC, TBP-HNO3 and RE MIX oxides (MIX) can be set.

On the left (upper part), there is a control valve for CO_2 discharge and the sample collection system.
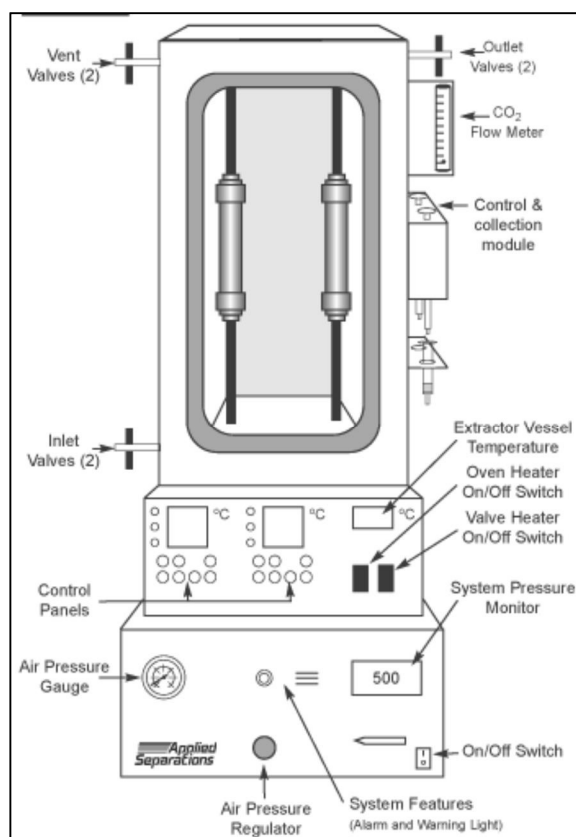

Figure 1: Experimental CO2-SC extraction plant

Usually, 15 min are required for cleaning the plant by static presence of CO2-SC in the extraction vessel using the same pressure and temperature settings used in the extraction experiment. After this, the CO2 discharge (6 ml/min flux) completes the cleaning in few minutes. The cleaning is followed by the vessel preparation for the extraction. The extraction is prepared putting in the vessel 1 cm of glass-whole, a circular paper filter on the vessel bottom, and attaching the vessel bottom to the CO2-SC circuit; than sequentially 10 ml of TBP-HNO3 and MIX (the weight varies experiment by experiment) are put in the vessel, after another circular paper filter is put on the vessel top before ceiling the vessel for the extraction.

After this, the extraction can be performed in static and/or dynamic conditions.

The static conditions involve the filling of the vessel with CO2-SC (setting the temperature, the pressure and the contact time) and the final discharge of CO2-SC and TBP-HNO3 containing the extracted RE. The dynamic conditions involve a continuous flow of CO2-SC in the vessel (setting also how much fast has to be the flow). In this work only the static conditions have been tested.

During the extraction, the static contact time between CO2-SC, TBP-HNO3 and MIX, is a studied variable of the system.

At the end of the contact time, the CO2-SC (containing the TBP-HNO3 and the MIX) is discharged and stored in a glass vial (shown in figure 2) containing 10 ml of Kerosene (the collected sample is an organic phase that consists of 20 ml, 10 ml TBP-HNO3 + 10 ml Kerosene).

Figure 2: Glass vial to collect reaction products.

2.2 Materials and equipment

- TBP (Ter-n-butyl phosphate) anhydrous min 98% (RPE)
- HNO_3 15M, 3M, 2M, 1M (RPE)
- HCl 6M (RPE)
- Iso-propyl alcohol (RPE)
- Kerosene (RPE)
- Oxalic acid bi-hydrated (RPE)
- Demineralized water (MilliQ)
- Rare earths oxides MIX-1 (weight composition: Y_2O_3 18,6%, Eu_2O_3 25,77 %, Nd_2O_3 18,83%, La_2O_3 20,03 %)
- Rare earths oxides MIX-2 (weight composition: Y_2O_3 23.65% , Eu_2O_3 22.67%, Nd_2O_3 18.31%, La_2O_3 23.13%)
- Flasks, Beakers, centrifuge plastic tubes, volumetric pipettes, magnetic stirrers, paper filters ash-less, separator funnels, desiccators
- Heating magnetic plate, centrifuge, analytical balance
- Thermostatic stove, muffle, vacuum pumps
- Thermometers
- Karl-Fisher titrator
- Densitometer DA110M
- CO2-SC plant "Spe-ed SFE-2" - Applied Separations
- ICP-OES Perkin Elmer

2.3 Methods

2.3.1 TBP-HNO₃ preparation and characterization

As reported in literature [1-5, 7, 8, 11, 17-23, 27-32] the same kind of ligand and the same volume (10 ml) was used for all the experiments.

The method for its preparation is described below.

At room temperature, 60 ml of anhydrous TBP and a magnetic stirrer, are placed in a 250 ml Pyrex flask. While the TBP is under stirring, slowly 60 ml of HNO3 15M (ca 67% weight) are added to the flask, and this

MIX is stirred for 30 min, than centrifuged (4000 RPM) for 60 min. The organic upper phase is picked up and added with 17.5 ml of anhydrous TBP obtaining thus the TBP-HNO3.

TBP-HNO3, just prepared, must to be stored in a dark and cold place, sealed in a glass bottle.

TBP-HNO3 was characterized measuring the density d (g/ml) and the water content W% (weight percentage):

$d_{25°C, TBP-HNO3} = 0.943 \pm 0.005$ g/ml

W% = 2.4% ± 0.2%

These measures were performed on three TBP-HNO3 differently aged samples (1 month, 15 days, 1 day) obtaining the same values. This prove that fresh TBP-HNO3, stored as just described, is stable.

Below are reported the same data also for the others reagents:

anhydrous TBP (starting reagent) - $d_{20°C} = 0.982$ g/ml (MSDS data), W% = 0.34 ± 0.05 (measured);

Kerosene (collection reagent) – d = 0.8 g/ml (MSDS data), W% ≈ 0 (measured);

2.3.2 Stripping of the organic phase (kerosene – TBP-HNO3).

The stripping procedure, [1-5, 7, 8, 11, 17-23, 27-32] , leads to the retro-extraction of the extracted RE (collected in the organic phase) in an acidic aqueous phase ready for the analytical steps.

At 50 °C and under magnetic stirring, the 20 ml sample (TBP-HNO3 + Kerosene) are placed with 20 ml HNO3 3M in a 250 ml Pyrex flask for 15 min. Then, under stirring and at checked temperature, slowly are added 100 g of demineralized water going on with the retro-extraction for additional 15 min. At the end of these two 15 min steps, stopping the stirring, are visible 2 phases (the upper one organic, the other aqueous) which have to be well separated in a centrifuge (4000 RPM for 15 min). The aqueous phase can be directly (or, if it is necessary, after dilution) analysed. The residual presence in RE in the organic phase can be tested by analysis, passing through the Oxalates precipitation procedure below reported.

2.3.3 Oxalates precipitation procedure

This procedure (here normalized to 100 ml of organic phase), through the precipitation of RE oxalates, after a muffle step, leads to almost pure RE oxides and allows close to 100% yields. It is applicable, either directly on TBP-HNO3 extracts, or on the TBP-HNO3 +Kerosene organic phase collected at the end of the CO2-SC assisted extraction process.

In a 1000 ml Pirex flask are placed 100 ml of organic phase with 100 ml of iso-propyl alcohol. The product by stripping procedure, heated under magnetic stirring to 60 °C, is slowly added with HCl 6M (10 ml), demineralized water (400 ml), Oxalic acid bi-hydrated (25 g added in low amounts). All this operations require 30 min. This MIX has to rest for 24 h (in this time the oxalates precipitate). The precipitate absence means the absence in RE.

Oxalates precipitates have to be filtered on paper ash-less filters and washed with Iso-propyl alcohol and water. Than the filter with the washed precipitates has to be put in a porcelain capsule, dried in stove (2h, 150 °C), mineralized in muffle (1h, 600°C) and finally cooled to room temperature in a desiccator.

After weighting procedure (at room temperature on an analytical balance subtracting the capsule weight from the whole, oxides plus cup weight) the RE content (and the single elements relative presences) of obtained oxides can be evaluated by ICP-OES analysis (displayed in the next paragraph).

2.3.4 ICP-OES analysis (by the analytical system: Perkin Elmer Optima 2000DV)

The optic part of the instrument is constituted by a double monochromator Echelle with two CCD detectors that are backlit and cooled. The nebulizer chamber is a Scott type with cross flow geometry.

The calibrations were performed by using the external standard method with 3 levels of concentration, covering two concentration decades, and subtraction of the blank.

To calibrate a solution of certified RE matrix with 2% HCl (ISO Guide 31, ISO Guide 35, Eurachem / CITAC Guide) at known concentration was injected and, if necessary, it were also used a multi-elemental MIX obtained starting from single element certified standards.

The chosen wavelengths, listed in table 1 (at least one for element), usually are not interferences affected. If any doubt occurs, more than one wavelength are used for the same element, thus in the mediate signal the interference error is minimized.

The instrumental parameters used during the analysis are summarized below:

➢**RF Power [W]:** 1400

➢**Plasma gas flow [L/min]:** 15 (Argon purity >99,996%)

➢**Plasma emission detection:** axial and/or radial

➢**Aux gas flow [L/min]:** 0.75 (Air)

➢**Neb. Gas flow [L/min]:** 0.5 (Nitrogen purity> 99,999%)

➢**Pump rate [ml/min]:** 1.5

➢**Eq. time [sec]:** 20

➢**Sample flush time [sec]:** 10

➢**n. replicates:** 3

➢**Dilution:** 125-1000

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> **Linearity range [r2]** >0,99998

> **Point of calibration:** 3

> **Background correction:** 2 point(subtraction of blank)

ELEMENT	Analytical wavelengths
Yttrium (Y)	371.029 / 361.104 / 324.227
Gadolinium (Gd)	376.839
Dysprosium (Dy)	394.468
Erbium (Er)	337.271
Samarium (Sm)	388.529
Ytterbium (Yb)	289.138
Holmium (Ho)	345.600 / 339.898
Terbium (Tb)	350.917
Europium (Eu)	381.967 / 412.970
Thulium (Tm)	313.126 / 346.220 / 384.802
Lutetium (Lu)	261.542

Table 1: Wavelengths chosen for the ICP-OES analysis.

2.3.5 Extraction without CO2-SC at room temperature.

The yield improvement due to CO2-SC was evaluated comparing the data reached and the data obtained without CO2-SC with the method described below in this paragraph.

In a 100 ml Pyrex flask was placed the RE Oxides MIX (or another matrix containing RE) with 10 ml of TBP-HNO3 and with a magnetic stirrer, and finally the flask was placed on a stirring/ heating plate.

The RE oxides weight, the extraction temperature, the extraction time were fixed at the same values of CO2-SC experiment to be compared.

After the extraction were added 10 ml Kerosene and this organic phase was treated with the upper described procedures till the analysis.

2.3.5 MIX preparation and characterization.

All the experiments were performed using a MIX of 4 RE oxides. La_2O_3, Nd_2O_3, Eu_2O_3, and Y_2O_3 (granulometry ≤ 40 μm) powders were strongly mixed in the right amount obtaining the MIX tested in the CO2-SC plant.

In this way were prepared two MIX:

- MIX-1 (weight composition: Y_2O_3 18,60%, Eu_2O_3 25,77 %, Nd_2O_3 18,83%, La_2O_3 20,03 %)
- MIX-2 (weight composition: Y_2O_3 23.65% , Eu_2O_3 22.67%, Nd_2O_3 18.31%, La_2O_3 23.13%)

The composition was tested by ICP-OES Analysis on 3 amounts of every MIX.

3. Results and discussion

3.1 Preliminary information

Due to the number of variables involved in this process, not all the parameters and working conditions have been optimized yet (e. g. the CO_2 pressure in the system, the CO_2 discharge control valve temperature, the plant washing conditions, etc..), so some minor parameters and working conditions have been chosen as reported in the publications and/or in the manuals.

Trying to optimize the procedures, before described, were performed several tests on the MIX varying extraction/contact time, amount of oxides used in the reaction and extraction temperature.

Moreover it is necessary to emphasize the complexity of the steps required to carry on the research. The figure 3 shows a flowsheet that summarizes this complexity.
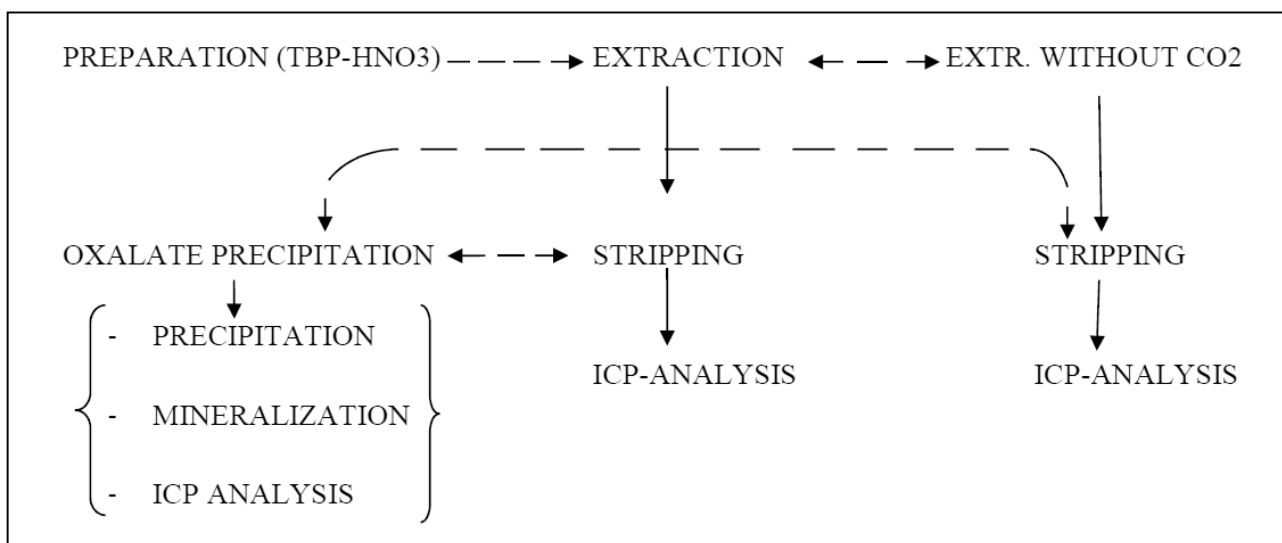

Figure 3: flowsheet reporting the working steps needed for the achievement of the data.

In addition to the usual flow line (the central one), the other ones are really important to validate the experiments and to plan new trials.

Obviously this experimental work leads to manage a lot of variables and the analytical results are reached at the end of many complicated steps influenced by many sources of errors.

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So it was necessary to be very careful and to achieve many replicates. Moreover for all the data here reported and discussed con be estimated a 10% error.

3.2 Effectiveness of CO2 assisted extraction.

Were compared two extraction experiments in which the same amount of MIX-1 (160 mg) was extracted with and without CO2-SC. The extraction with CO2-SC was performed using the EXC conditions: plant settings displayed in 2.1 paragraph, 50 °C oven temperature, 150 bar CO2 pressure, 1h contact/extraction time. In the table 2 are scheduled the results for 160 mg of MIX-1, extracted using the EXC conditions:

160 mg Oxides MIX-1		
Element	% yields	
	with CO2	without CO2
La	50	22
Nd	79	62
Eu	92	90
Y	66	23

Table 2: Yields for the MIX-1 extraction.

The same extraction/comparison experiments were also performed using 1000 mg of MIX-1.

In this latter case the "without CO2" yields appear to be higher than the other ones.

This let to think that, even if 10 ml of TBP-HNO3 (either with 160 mg, or with 1000 mg) are theoretically able to extract all the RE in excess, when there is CO2 reacta only a fraction of TBP-HNO3 (this argument is further discussed in the incoming paragraphs).

This is not influent when the TBP-HNO3 excess is higher (160 mg), but could become influent in presence of higher amounts of MIX-1. A theoretical calculation of the real amount of TBP-HNO3 really ready to react during the CO2 assisted extractions is shown in the next paragraphs.

3.3 Evaluation of the effect of the weight of MIX extracted.

The experimentation session, on the effect of the MIX weight, was performed with the MIX-2 (this new MIX preparation was necessary because the MIX-1 expired during the "contact/extraction time" experiments session) and using for every experiment a new seals set (increasing the MIX weight putted in the extraction vessel there were more losses in the plant).

Different amounts of MIX-2 were tested using the EXC conditions (180 mg, 250 mg, 400 mg, 700 mg, 1000 mg, 1500 mg, 2000 mg).

The figure 4 shows the yields achieved increasing the MIX-2 weight.

Increasing the weight over 400 mg, all the yields showed a decreasing path. Eu has an high constant yield till 400 mg, than the yield falls down and becomes again constant (and low) in the range 1000-2000 mg. Similar path has Nd (with lower yields). The Y and La show a proper linear decreasing path.
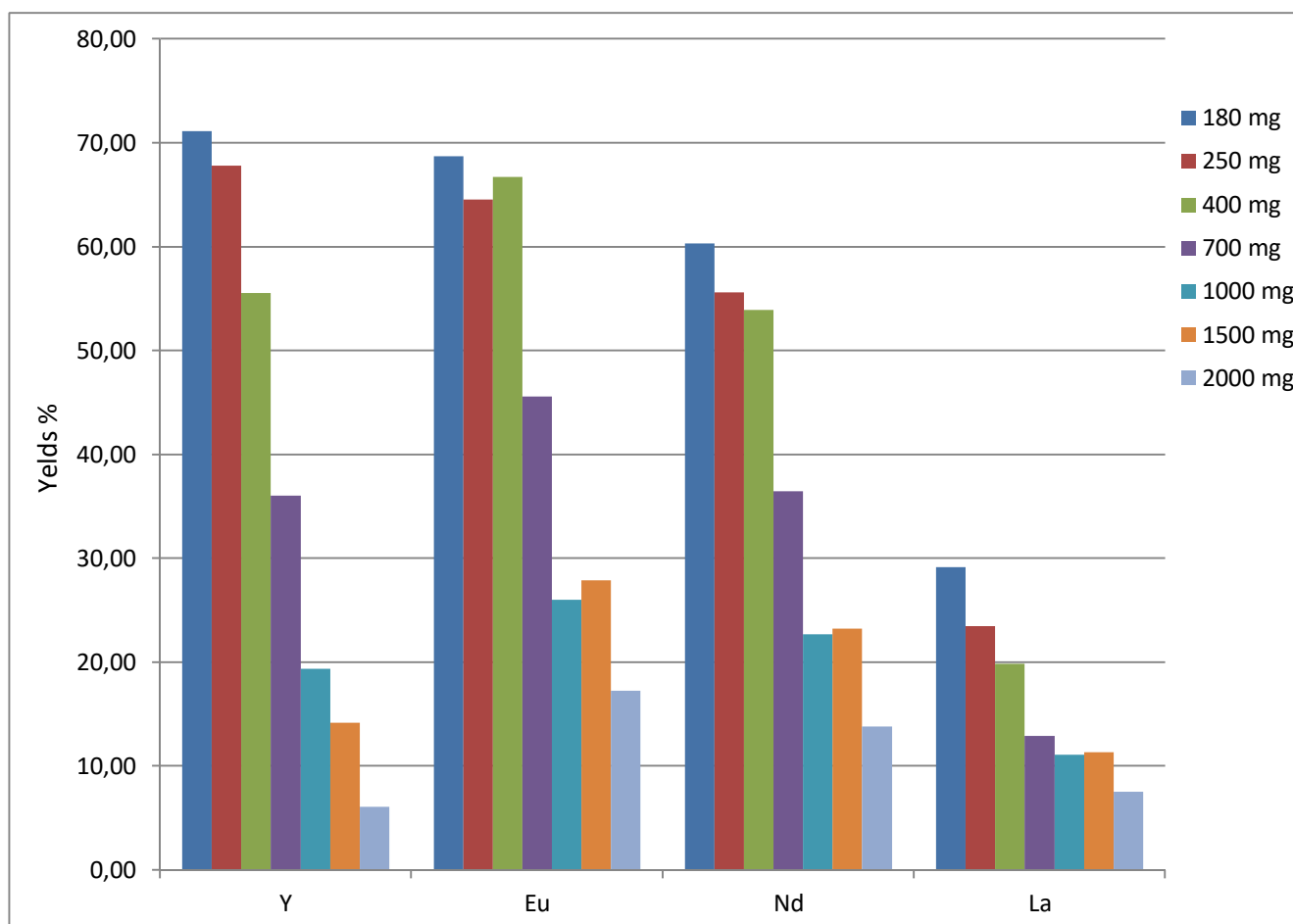

Figure 4 ó Achieved yields increasing the MIX-2 weight

The different paths are clearly shown in the figure 5, in which a 3D representation shows õbaseball capö shaped surface. As reported in the 3D graph, for the Eu and the Nd, the yields, starting from 1000 mg and till 2000 mg, decrease slower than Y and La.

Another visual that further and better explains this matter is in figure 5 in which there is a cut of the õbaseball capö for every RE.
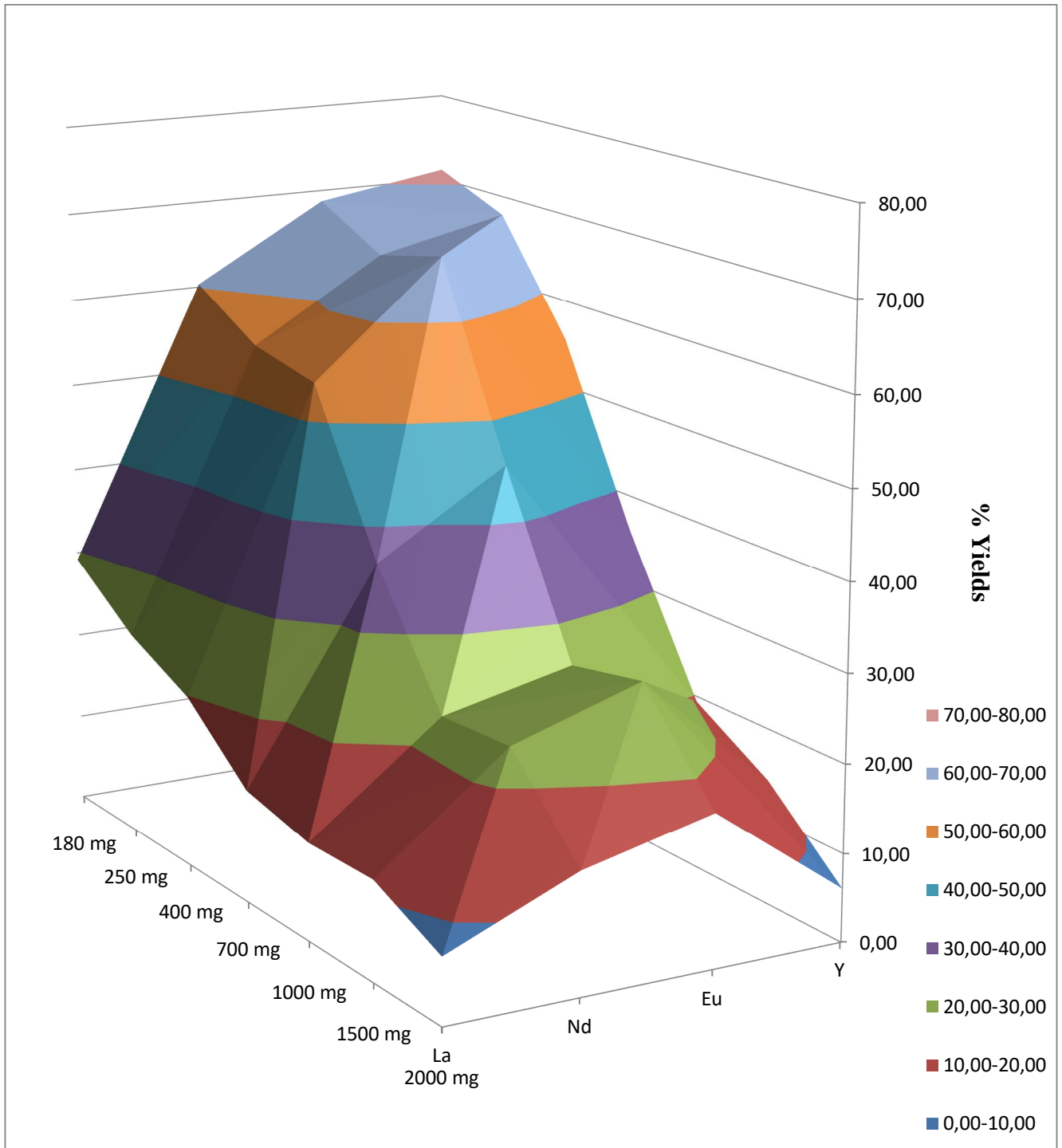

Figure 5 ó 3D õbaseball capö shaped surface reporting, the paths of the yields versus the MIX-2 mg extracted, for four RE.
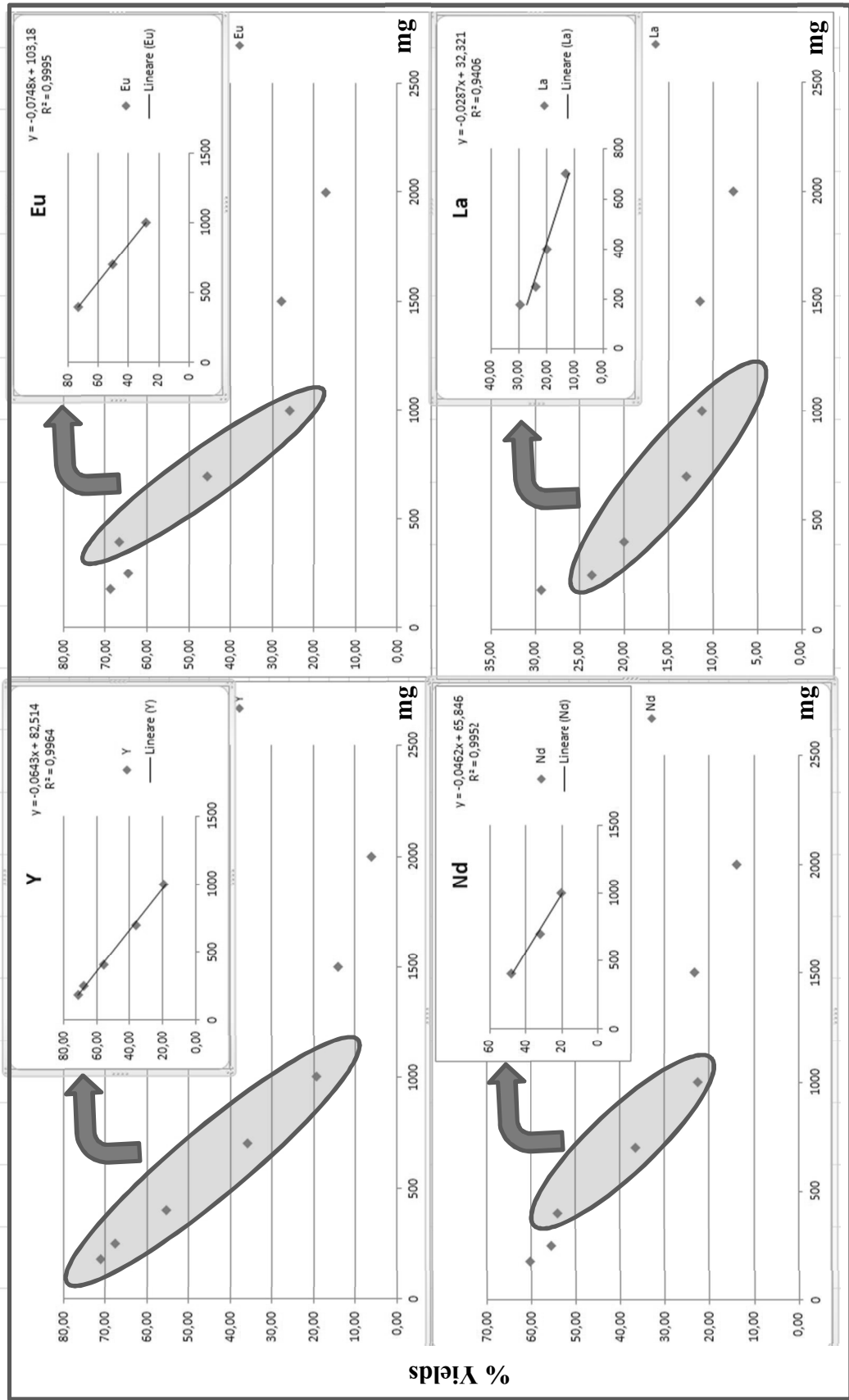
Figure 6 – Linear fittings between yield and MIX weigh

The weight range 400-1500 mg should be better investigated because in that range probably our extraction system approaches the saturation and, within the saturation conditions, the system seems to prefer the creation of more stable coordination complexes with Eu and Nd.

The ratio between the total amount of milli-moles extracted (for every weight put in the extraction vessel starting from 180 mg and till 2000 mg) and the (constant) total amount TBP milli-moles contained in 10 ml of the TBP-HNO3 ligand, are reported in the graph of figure 7.

The graph shows that in the range 400-700 mg of the system is saturated and that approximatively 25-30 molecules of TBP are necessary for every RE atom.
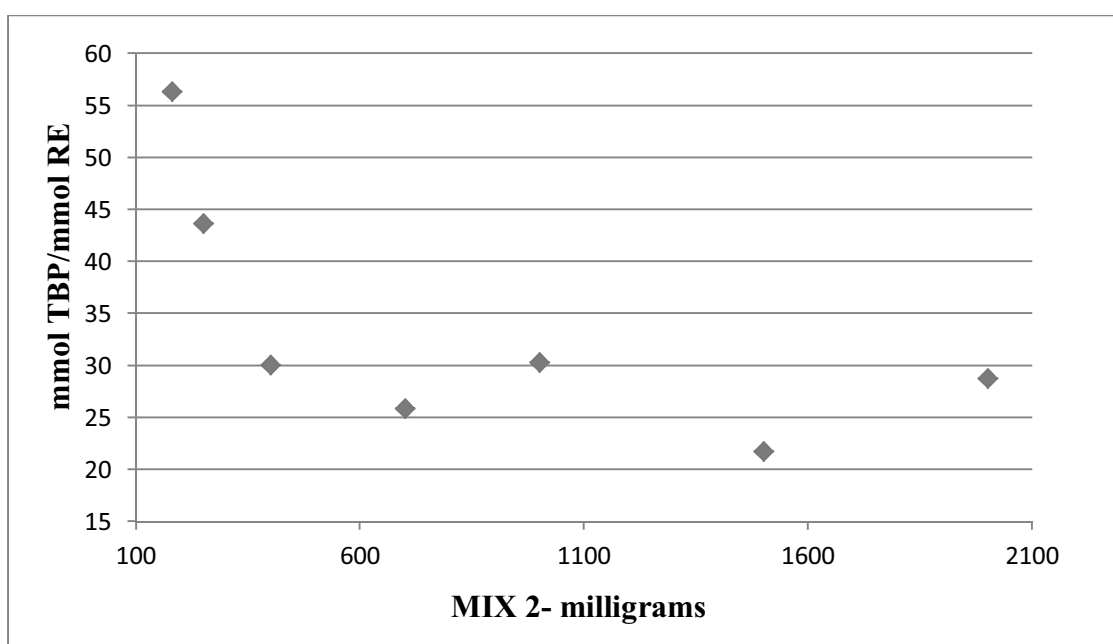

Figure 7 – Ratio [total mmol TBP-HNO3 (10 ml) / total RE mmol extracted] , versus MIX-2 milligrams putted in the vessel.

At the end of every extraction experiment into the extraction vessel there was a residual powder. For the 180 mg and the 2000 mg experiments this powder was collected (using hot acids) and analysed by ICP-OES. The analytical data fit the mass balance confirming that the retro-extraction displayed in the stripping procedure (paragraph 2.3.1) is quantitative.

3.4 Evaluation of the effect of the static contact/extraction time between CO2-SC and the MIX.

By using always the EXC conditions and the same amount of MIX-1 (160 mg) at different static contact time (10 min, 30 min, 40 min, 60 min, 80 min, 120 min) were tested.

As displayed in the figure 8 **Eu is always almost fully extracted (also for short contact time)** and, starting **from 40 min, of the yields for the other elements appear to be constant** and not linked to the contact time contact time (yields: La é 45%, Nd é 90%, Eu and Y é 100%).
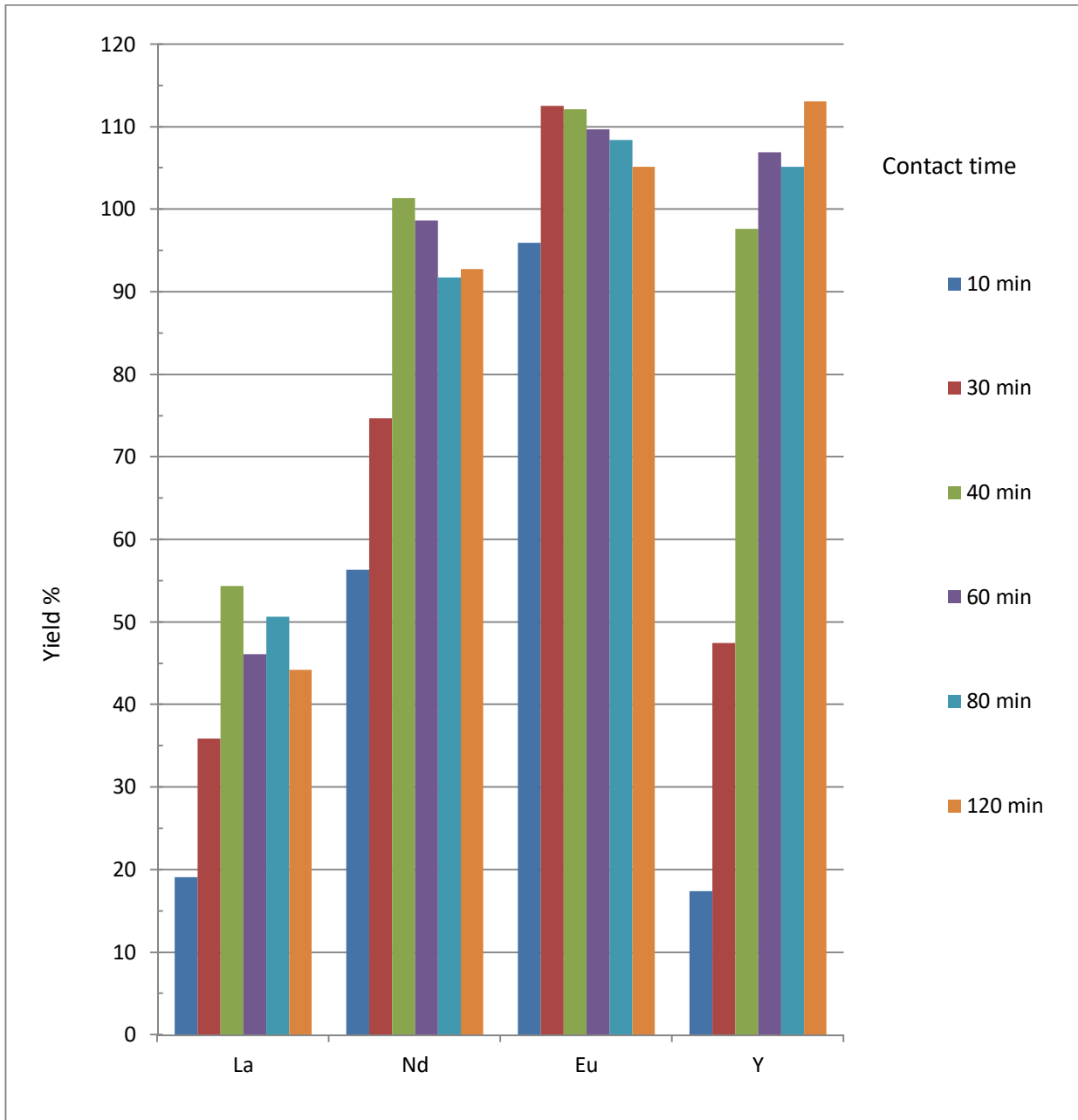

Figure 8 ó Achieved yields increasing the contact time

In the figure 9 are reported the linear fittings between yield and contact time in the range 0 - 40 min.

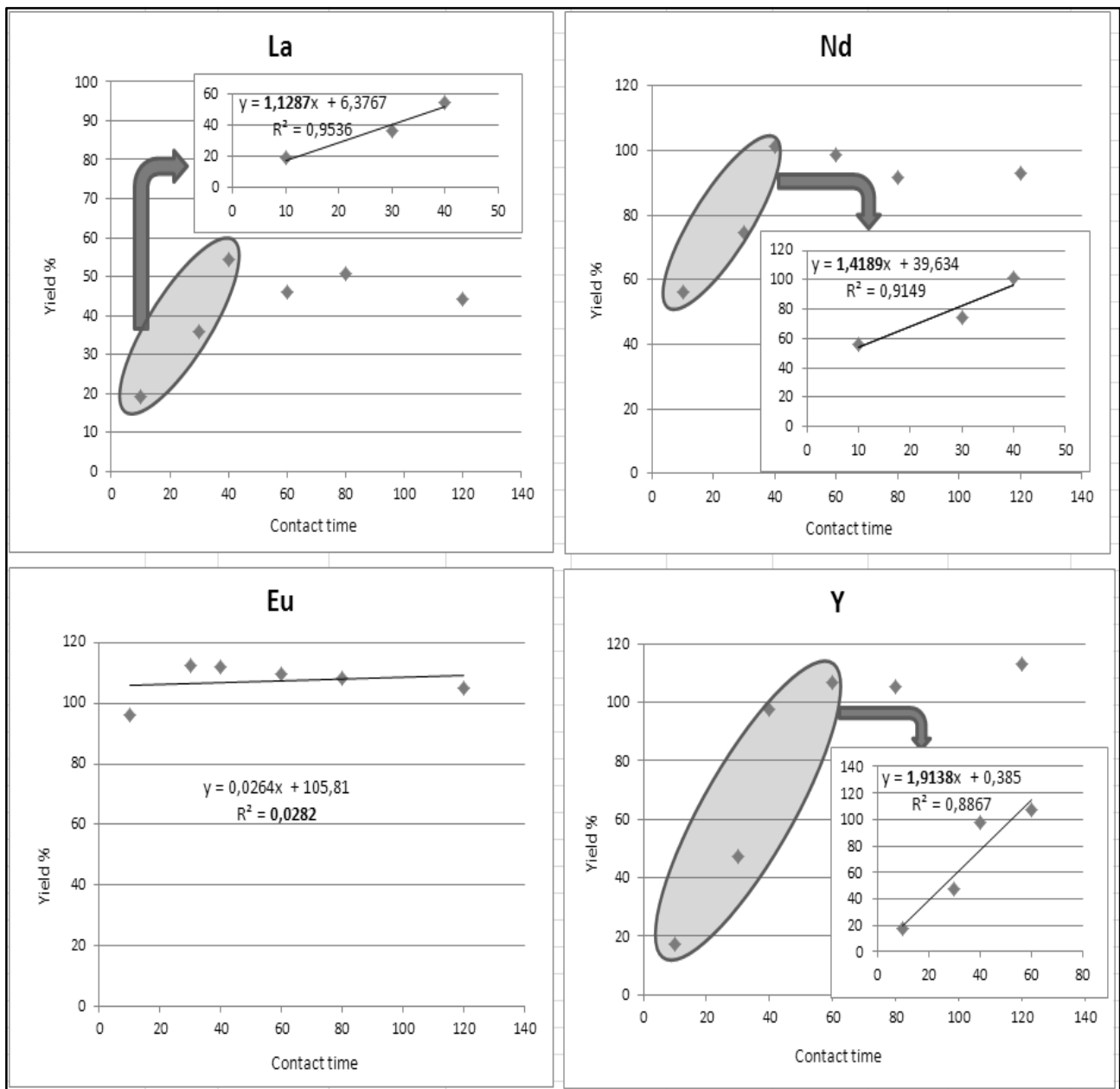**Figure 9** – Linear fittings between yield and contact time

Looking at the data, some conclusions (useful also for industrial applications) could be pulled out.

The partial extraction of La (the maximum yield registered is ca 50%) is related to the residual powder found in the reaction vessel at the end of every extraction. The La content, in this powder, could be used for its separation and purification.

Working on the fast extraction of Eu and on the differences among the RE slopes (Yield % vs Contact Time), it could be possible to project a new plant and a new process for the RE separation and purification.

3.5 RE oxides powder from luminescent material in waste fluorescent lamps (ELMIX).

As requested by TIAG, we made a short trial to test a real matrix (a powder containing RE oxides and other oxides provided by TIAG whose analytical data are reported in Figure 10). This test was performed in EXC conditions, 1 h static contact time with 250 mg of ELMIX.

Analysenbericht zu Auftrag: A - 45020				Seite 2 von 2 A-45020
SE-AL ICP		Wert	EH	Erw.: min/max/typ
Na2O	%	9,44	%	//
Al2O3		850	ppm	//
BaO		76	ppm	//
Bi2O3		2	ppm	//
CdO		<2	ppm	//
Co3O4		<7	ppm	//
Cr2O3		<7	ppm	//
CuO		8	ppm	//
Fe2O3		272	ppm	//
MgO		25	ppm	//
MnO2		6	ppm	//
Nb2O5		<14	ppm	//
NiO		6	ppm	//
PbO2		6	ppm	//
Sb2O3		85	ppm	//
SiO2		86	ppm	//
SnO2		3	ppm	//
SrO		56	ppm	//
ThO2		<1	ppm	//
TiO2		<8	ppm	//
U3O8		<1	ppm	//
V2O5		<9	ppm	//
ZnO		56	ppm	//
CeO2 / GOSE		0,1	%	//
Dy2O3 / GOSE		<0,1	%	//
Er2O3 / GOSE		<0,1	%	//
Eu2O3 / GOSE		6,1	%	//
Gd2O3 / GOSE		1,8	%	//
Ho2O3 / GOSE		<0,1	%	//
La2O3 / GOSE		0,9	%	//
Lu2O3 / GOSE		<0,1	%	//
Nd2O3 / GOSE		<0,1	%	//
Pr6O11 / GOSE		<0,1	%	//
Sm2O3 / GOSE		<0,1	%	//
Tb4O7 / GOSE		<0,1	%	//
Tm2O3 / GOSE		<0,1	%	//
Y2O3 / GOSE		91,0	% berechnet	//
Yb2O3 / GOSE		<0,1	%	//
CaO		0,24	%	//
SE-AL NCH		Wert	EH	Erw.: min/max/typ
GOSE		82,9	%	//

Figure 10 – Analytical data of the ELMIX powder

The same amount of ELMIX (250 mg) was extracted for 1 h in a stirred flask without CO2-SC at room temperature as reported in paragraph 2.3.4.

As below displayed (figure 11) only 4 RE (La, Gd, Eu, Y) were detectable and for every RE the yields (with and without CO2-SC) were almost the same (only for La there was a difference).
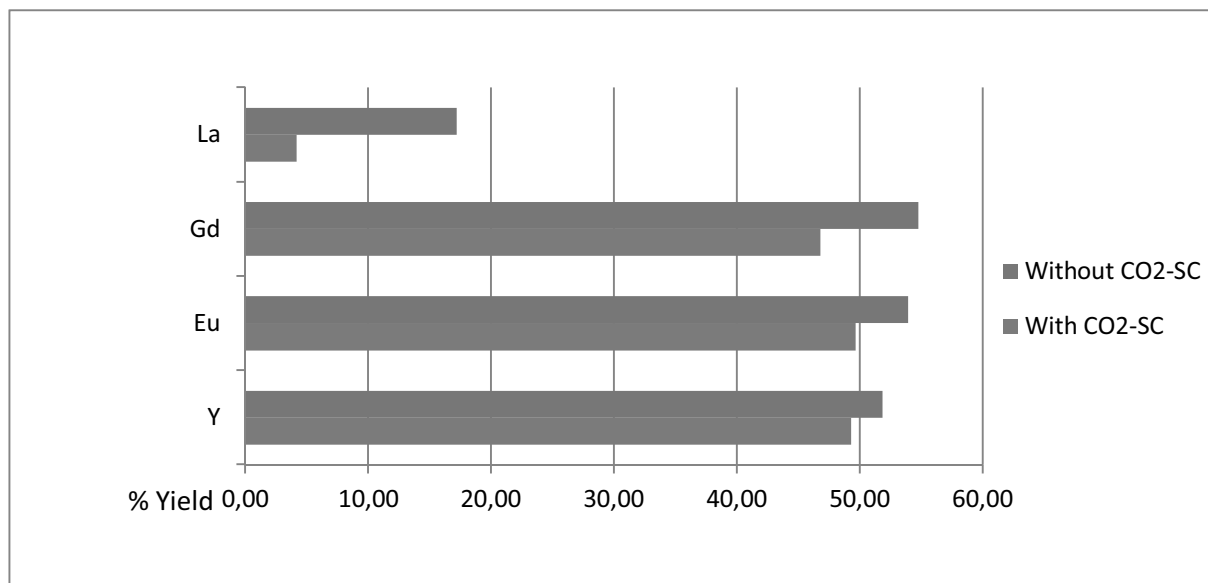

Figure 11 – Extraction yields on ELMIX with and without the use of CO2-SC

In addition to the extraction experiment, the analysis of 6 elements (Na, Al, Ba, Sb, Fe, Ca - in bold the trivalent ions) were also performed on the 20 ml of the extraction sample (composed by Kerosene-TBP-HNO3) treated with the stripping procedure (reported in 3.1 paragraph). These 6 elements have been chosen because they are the only ones detectable by our instrument. In both the samples (with and without CO2-SC) these 6 elements were almost absent. The only unexpected data was the Ca concentration detected. Indeed its concentration was threefold the maximum possible concentration in every sample (we theorize a contamination by used chemicals). Comparison of these data with that obtained in MIX-1 trials is not easy due to the difference in RE composition because the presence of other oxides could influence the extraction. Anyway some considerations could be done:

1) the competition, by using TBP-HNO3 extraction, between RE and other trivalent ions could be excluded,

2) the RE extraction lead to an almost pure aqueous solution containing RE,

3) in the final aqueous extracted solution probably could be performed also a separation and purification of the RE.

4. Conclusions

The experimental work leads to manage a lot of variables. The analytical results are at the end of many complicated steps and every step is influenced by many sources of errors.
So it's necessary to be very careful and to achieve many replicates.

The analysis of the organic phase (containing TBP-HNO3 and Kerosene) residual after the stripping procedure (2.3.1 paragraph) performed after the precipitation procedure (2.3.2 paragraph) shows that the RE are almost absent in this phase resulting almost completely extracted in the stripping aqueous phase.

The not complete extraction of the RE in the CO2-SC assisted extraction experiment it's confirmed by the presence, in the vessel, of some residual MIX powder. This powder, collected and analysed, fits the mass balance confirming that the retro-extraction displayed in the stripping procedure (paragraph 2.3.1) is quantitative.

Looking at the contact time effect, approaching the best separation and purification, could be used the differences among the RE slopes (Yield % vs Contact Time) in the range 0-40 min. Is also good promising the use of the low extractability of La (the maximum yield registered is ca 50%) and the fast and high extractability of Eu.

Similarly, studying the weight effect it could be useful, approaching the best separation and purification, to pay attention on the differences among the RE slopes (Yield % vs weight) in the range 0-400 mg. Also interesting is the investigated saturation range 400-2000 mg in which, increasing the MIX-2 weight, there was a quite linear yield decreasing for Y e La in spite of the quite constant yields registered for Eu and La.

The just obtained ELMIX data open a new research field. The data collected (first of all the absence of not RE elements in the TBP extract) are promising good but better result could be obtained only if the extraction mechanisms will became clearer.

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