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Recovery of the Rare Metals from Various Waste Ashes with the Aid of Temperature and Ultrasound Irradiation Using Chelants

Hiroshi Hasegawa,*[, 1] Ismail M. M. Rahman,*[, 2, 3] Yuji Egawa,[3] Hikaru Sawai,[3] Zinnat A. Begum,[3] Teruya Maki,[1] and Satoshi Mizutani[4]

[1]*Institute of Science and Engineering, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan*

[2]*Department of Applied and Environmental Chemistry, Faculty of Science, University of Chittagong, Chittagong 4331, Bangladesh*

[3]*Graduate School of Natural Science and Technology, Kanazawa University, Kakuma, Kanazawa 920-1192, Japan*

[4] *Graduate School of Engineering, Osaka City University, Sugimoto 3-3-138, Sumiyoshi-Ku, Osaka 558-8585, Japan*

*Author(s) for correspondence.

E-mail: hhiroshi@se.kanazawa-u.ac.jp (H. Hasegawa); I.M.M.Rahman@gmail.com (I.M.M. Rahman).

Tel/ Fax: +81-76-234-4792

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Abstract

The incineration fly ash (IFA), molten fly ash (MFA), thermal power plant fly ash (TPP-FA), and nonferrous metal processing plant ash (MMA) have been screened in terms of the following *rare*-termed metal contents: B, Ce, Co, Dy, Eu, Ga, Gd, Hf, In, Li, Lu, Mn, Nb, Nd, Ni, Pr, Rb, Sb, Se, Sm, Sr, Ta, Tb, Te, Ti, Tm, V, W, Y, and Yb. The pseudo-potential for recycling of the waste ashes, as compared to the cumulative concentration in the crust (mg kg^{-1}), was determined as follows: MMA > IFA > MFA > TPP-FA. The comparison with the crude ore contents indicates that the MMA is the best resource for reprocessing. The recovery of the target metals using aminopolycarboxylate chelants (APCs) has been attempted at varying experimental conditions and ultrasound-induced environment. A better APC-induced extraction yield can be achieved at 0.10 mol L^{-1} concentration of chelant, or if the system temperature was maintained between 60 to 80 °C. Nevertheless, the mechanochemical reaction induced by the ultrasound irradiation has been, so far, the better option for rare metal dissolution with chelants as it can be conducted at a minimum chelant concentration (0.01 mol L^{-1}) and at room temperature (25±0.5 °C).

Keywords: Rare metals; Recovery; Fly ash; Solid waste; Aminopolycarboxylate chelant; Ultrasound irradiation

1.0 Introduction

The consumption rates of the metals are continually increasing due to the diversification in applications. On the contrary, the supply of metals becomes more and more limited because the resources are nonrenewable (Guinée et al. 1999). The natural deposits of some metals, which have been increasingly consumed as a key material in clean energy applications or in designing alluring daily life gadgets, are unevenly distributed in the world and have an unsteady supply chain or fluctuating market price according to the policy of the resource country (Dodson et al. 2012, Massari & Ruberti 2013). The terminology, rare metal, is thus introduced to interpret such metals, which is not an academically defined one, and there is no consensus on which element it pertains (AIST Rare Metal Task Force 2008, Kooroshy et al. 2010). For example, in Japan, 31 ores, including the rare earth elements as a group, have been designated as rare metals in terms of the concern in securing a stable supply of resources (Kawamoto 2008). Consequently, other than the refinery production, the reclaim processing of rare metals from secondary resources, such as process discards from the rare metal-consuming manufacturing schemes (Hsieh et al. 2009, Liu et al. 2009, Kang et al. 2011, Li et al. 2011, Park 2011, Virolainen et al. 2011, Hasegawa et al. 2013b) or end-of-life electronic products (Shimizu et al. 2005, Cui & Zhang 2008, Rabah 2008, Bertuol et al. 2009, Binnemans et al. 2013, Hasegawa et al. 2013c, Hasegawa et al. 2013a), received sincere focus from the researchers.

Municipal solid waste (MSW) management is in crisis in many of the world's largest urban areas as populations are continued to grow, which creates an increase in the waste quantities, while disposal places, such as sanitary landfills around the periphery of the cities, are decreasing. The alternative approach that has caught the attention of decision makers is the mass burn incineration that is increasingly practiced in the OECD (Organisation for Economic Co-operation and Development) countries (Anonymous 1999). Moreover, the thermal treatment of MSW not only reduces the amount of waste to be landfilled, but also allows the waste hygienization (Sabbas et al. 2003). Due to the effectiveness of policy

implementation, the trends of landfill and incineration for MSW processing are respectively decreasing and increasing in the high-income countries (Mazzanti & Zoboli 2008). The potential of waste ashes (viz., fly ash and bottom ash), a reaction by-product of the MSW incineration treatment, is anticipated as a secondary resource for rare metals, because the electronic wastes have become the foremost stream of MSW in recent years (Jung et al. 2004, Babu et al. 2007, Kim et al. 2009, Ogunseitan et al. 2009, Hossain et al. 2012).

The MSW management scenario of Japan has been taken into account as a representative scenario of the high-income countries in the current work. It has been estimated that Japan produces about 50 million tons of MSW per annum followed by the incineration treatment of an approximate 77% of the total and produces both fly ash and bottom ash (Jung & Osako 2009). A further contribution in the fly ash total added from the melting treatment of the incineration residues, as practiced in Japan, which is known as molten fly ash (Alorro et al. 2009). The elemental characterization of the incinerator ashes representing unalike resources indicates the presence of a considerable proportion of rare metals (e.g., Y, La, Ce, Pr, Nd, Dy, Yb, Ho, Er, Tm, Lu, Ag, Bi, Ga, Ge, Pd, In, Sb, Sn, Te, and Tl) other than the toxic base metals (Zhang et al. 2001, Jung et al. 2004, Jung & Osako 2009). The coal fly ash produced during the coal processing has also been characterized with the enriched presence of several valuable elements, such as Ge, Ni, Ga, and V (Font et al. 2005, 2007). Leaching via acidic and alkaline treatments, followed by a subsequent step of metal recovery from leachates involving either solvent extraction, selective precipitation, or solid-phase separation (Tsuboi et al. 1991, Vitolo et al. 2000, Font et al. 2007, Navarro et al. 2007, Yang et al. 2010), and vapor phase extraction (Murase et al. 1998) is attempted to reclaim rare metals from the waste ashes.

The present study discusses the comparative recycling potential of the representative ash types in terms of the rare metal content from the direct incineration of MSW, the melting treatment of the incineration residues, the coal combustion in the thermal power plants, or the smelting plants of nonferrous metals. The work also includes investigation of the reclamation

of rare metals from the real waste ashes at varying conditions with the use of aminopolycarboxylate chelants (APCs), which has not been carried out before.

2.0 Experimental

2.1 Materials

2.1.1 Waste ash

The waste ash samples used in this study represent the following origin: (a) incineration fly ash (IFA) (S-1 to S-9), (b) molten fly ash (MFA) (S-10 to S-13), (c) thermal power plant fly ash (TPP-FA) (S-14 to S-18), and (d) nonferrous metal processing plant ash (MMA) (S-19). The IFA and MFA samples are from the MSW operations, while the TPP-FA or MMA samples have been collected from the respective operating plants situated in several different locations of Japan. However, the locations or names of the participating establishments have not been disclosed as per request from the responsible personnel of the organizations to avoid violating any corporate rules related to the information sharing policy.

2.1.2 Aminopolycarboxylate chelants

Disodium dihydrogen ethylenediamine tetraacetate dihydrate (EDTA), [S,S]-ethylenediaminedisuccinic acid (EDDS), and 3-hydroxy-2,2'-iminodisuccinic acid (HIDS) are the APCs used, which have been procured, respectively, from Wako Pure Chemical (Osaka, Japan), Chelest (Osaka, Japan), and Nippon Shokubai (Tokyo, Japan). Some general information about the APCs is listed in Table 1.

2.1.3 Other materials

Analytical reagent grade materials are used throughout. The PlasmaCAL multielement solutions in 5% HNO_3 from SCP Science (Québec, Canada) have been used as the standards during metal concentration measurements. The 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES) from Nacalai Tesque (Kyoto, Japan) has been used as the buffer reagent to maintain the solution pH at neutral conditions, while the HCl or

NaOH solution (1 mol L^{-1}) from Kanto Chemical (Tokyo, Japan) has been used for pH adjustment.

The low-density polyethylene bottles, perfluoroalkoxy tubes, and micropipette tips have been used as the laboratory accessories, which were purchased either from the Nalge Nunc (Rochester, NY) or Nichiryo (Tokyo, Japan). The careful cleaning of each of the laboratory wares has been performed with overnight soaking in an alkaline detergent (Scat 20X-PF; Nacalai Tesque, Kyoto, Japan) and then in HCl solution (4 mol L^{-1}; Kanto Chemical, Tokyo, Japan), followed by rinsing with ultrapure water after each of the aforementioned phases.

2.2 Instrumentation

The iCAP 6300 inductively coupled plasma optical emission spectrometer (ICP-OES) from Thermo Fisher Scientific (Waltham, MA) have been used to perform the metal analysis, which have been equipped with an EMT duo quartz torch, glass spray chamber, and concentric glass nebulizer. The RF power at the torch was maintained at 1.15 kW; the plasma gas flow, the auxiliary gas flow, and the nebulizer gas flow have been sustained, respectively at 12, 1 and 0.5 L min^{-1} and the integration time was 30 s.

The TOSOH 8020 high-performance liquid chromatography (HPLC) system from Tosoh (Tokyo, Japan) have been used to confirm the chelant concentration. A DP-8020 pump, an AS-8021 auto sample injector, a CO-8020 column oven, a PD-8020 UV-Vis detector, and the PD-8020 data processing software have been included within the assembly of the HPLC system. The TSK-gel ODS-80TM octadecylsilica columns (4.6 mm i.d. × 250 mm and 4.6 mm i.d. × 150 mm) have been used. The 5 mM solution of ammonium dihydrogenphosphate of pH 2.4 has been used as the mobile phase with a pumping flow rate of 0.5 mL min^{-1} at 25 °C. The injection volume was 20 μL, and the detection has been performed at 254 nm.

The Multiwave 3000 microwave reaction system from Anton Paar GmbH (Graz, Austria) equipped with 8-position rotor and hydraulic pressurized sensing system has been used for the acid-assisted solid sample digestion. The digestion vessels within the instrument

assembly are designed to sustain a controlled pressure of 6 MPa, maximum operating pressure of 12 MPa, and highest temperature of 2,600 °C.

The Navi F-52 pH meter from Horiba Instruments (Kyoto, Japan) with a combination electrode was the instrument for measuring the solution pH. The Arium Pro water purification system from Sartorius Stedim Biotech GmbH (Göttingen, Germany) was employed for preparing the ultrapure water of resistivity > 18.2 MΩ cm^{-1}, which has been used throughout for dilution or washing purpose.

2.3 Methods

2.3.1 Determination of rare metal content in the waste ashes

The ash samples (0.5 g) have been transferred into the pre-cleaned PTFE vessels of the microwave reaction system and mixed with hydrofluoric acid (5 mL), nitro-hydrochloric acid (5 mL), and 60% perchloric acid (1 mL) to conduct the digestion at 180 ± 5 °C for 2 h. The EPA method 3052, which is often recommended for the multielemental analysis, was followed for the sample preparation, reagent selection, and adjustment of the digestion conditions (EPA 1996, Kingston & Walter 1998). The digestion extracts have been separated from the residue (if any) using the assembly of a cellulose membrane filter (0.45 μm; Advantec, Tokyo, Japan) and an MAS-1 suction system (AS ONE, Osaka, Japan), which has been further treated at 60 °C to concentrate the volume to a few milliliters. The concentrated extracts have been finally diluted to a volume of 100 mL with ultrapure water and stored at 4 °C until the analysis. The reported values are averaged from at least three replicates of digestion of each of the ash samples.

2.3.2 Extraction of rare metals from waste ashes using chelants

The EDTA, EDDS, or HIDS solutions have been prepared at 0.01, 0.05, 0.10, and 0.15 mol L^{-1} concentrations, and the solution pH was adjusted at pH 7 with HEPES (0.1 mol L^{-1}). A control experiment was simultaneously performed using ultrapure water only. The pH-adjusted chelant solutions (10 mL) were added to the waste ash (0.1 g), and the mixtures have been shaken at a rotating speed of 240 rpm for 24 h in an end-over-end shaker at 25 ± 2 °C.

The suspension was then centrifuged at 3,000 rpm for 10 min using the Kokusan H-701FR centrifuge (Kokusan Corporation, Tokyo, Japan) and parted using the previously mentioned filtration assembly that consists of a cellulose membrane filter and an MAS-1 suction system. The filtered extracts were stored at 4 °C until the analysis.

2.3.3 Chelant-assisted extraction of rare metals under the influence of temperature or ultrasound irradiation

The effect of temperature changes or ultrasound (US) irradiation on the chelant-assisted rare metal extraction was checked using a mixture of chelant and ash waste prepared at a 100:1 ratio of chelant and ash. The Digiprep Jr. block heater from SCP Science (Quebec, Canada) has been used to create the varying temperature conditions within the range of 25 to 98 °C, and to maintain for 6 h. The US irradiation effect was generated using an UO 300 FB-P US bath from Kokusai Alpha (Toyama, Japan). A reaction vessel (50 mL) was placed in the center of the US bath and was sonicated for 6 h. The temperature was maintained at 25±0.5 °C.

The separation process of the supernatant from the solid residue and the storing conditions were the same as mentioned before. In each of the cases, the extractions were performed in triplicate with and without the chelant solutions, and an averaged value is considered.

3.0 Results and discussion

3.1 Characterization of the waste ashes

3.1.1 Rare metal loading in the waste ashes

The contents (mg kg^{-1}) of 30 rare-termed elements (B, Ce, Co, Dy, Eu, Ga, Gd, Hf, In, Li, Lu, Mn, Nb, Nd, Ni, Pr, Rb, Sb, Se, Sm, Sr, Ta, Tb, Te, Ti, Tm, V, W, Y, and Yb) in the 19 samples of different waste ashes (IFA, MFA, TPP-FA, or MMA) are compiled in Table 2. An utmost concentration of above 50 mg kg^{-1} has been commonly found for nine species of rare metals, which were as follows: B, Li, Mn, Ni, Rb, Sb, Sr, Ti, and W. The Ce loading in

the TPP-FA was above the 50 mg kg^{-1}, while it appeared at a low amount in the other ash variants. The Ta or Tm loading was below the limit of instrumental detection irrespective of the ash variants, and the Co and Hf were limited to S-15 and S-13, respectively.

The comparative distribution of rare metals in the waste ash types is illustrated in Figure 1 averaging the values attained for the samples of each ash type. The standard deviation values have not been included due to the discrete pattern of the sample population size. The MFA is the product of the melting treatment of the incineration-generated solid reaction by-products (bottom ash and fly ash) (Zhang & Itoh 2006), which supposed to result a higher content of metals in the MFA than that of the IFA. However, in the current work, in spite of the few instances that support the aforementioned hypothetical postulation (e.g., Ga, Ni, Rb, Se, Sr, Tb, and W), the common patterns indicated either lower or analogous concentration of metals in MFA in several cases. Some metals, such as Eu, Lu, and Nd, were remained below the detectable limit in the MFA even being present in the IFA. The nonexistence in correlation is attributable to the fluctuation in the composition of the incineration residues that used as the feedstocks in the melting furnaces. The data-sets for Ga, In, Sb, and Te element loading in the MFA manufactured from the incineration residues produced in Japan are available from the literature (Jung & Osako 2009), and a fairly similar pattern with the current work can be noted.

The dust produced during lead smelting operation (MMA) exclusively contains a significant amount of In, Se, and Te as compared to the other ash types. The contents of Ce, Gd, Li, Lu, Nb, Nd, Sr, V, Y, and Yb in the TPP-FA were higher than those of IFA, MFA, and MMA. The modern thermal power plants usually employ the coal gasification technique during operation, and the mode of occurrence of elements in gasification fly ash puts forward the possibility of utilization of the TPP-FA for recovery of a number of valuable elements, e.g., Ga, Ni, and V (Font et al. 2005).

3.1.2 Recycling potential of the waste ashes

The waste ashes, the fly ash, in particular, are practically delivered as a feed material in some refineries. However, the amount is not yet that significant, and the waste ashes are more commonly disposed of in landfills (Cobo et al. 2009). The respective crude ore quality (COQ) and concentration in the crust (COC) for each of rare metals (Halada et al. 2001) included in this study has been listed in the Table 1 to predict the recycling potential of the waste ashes.

In terms of the crude ore contents, the MMA seems to have the most potential among the waste ashes for commercial recycling. The In-loading value (23,534 mg kg^{-1}) is much higher than the content in the crude ore (10 mg kg^{-1}), and the Se content (2,997 mg kg^{-1}) is moderately comparable to the COQ value (2,000 mg kg^{-1}). The COQ values were either not available or not significant for comparison with the other metals. However, the COC values suggest the pseudopotential for recycling of at least 28 metals excluding the Ta and Tm. The recycling potential of the waste ashes has the following order (mg kg^{-1}): MMA (31,048 mg kg^{-1}) > IFA (10,810 mg kg^{-1}) > MFA (9,413 mg kg^{-1}) > TPP-FA (7,137 mg kg^{-1}), when compared with the cumulative values of COC (5,918 mg kg^{-1}).

The prime factor that gets in the way of recycling of waste ashes as a mineral resource is the uncertainty of composition, which includes the content of valuable metal species and detrimental components (Jung & Osako 2009). The metal loading (mg kg^{-1}) in the IFA from the hazardous waste incinerator in Medellin, Colombia, for certain rare metals (Mn 154.8, Ni 240.8, Sb 10465.2, V 5.9 and Yb 0.01) (Cobo et al. 2009) can be compared with the same reported in the current study (Mn 622.7, Ni 114.8, Sb 942.2, V 20.0 and Yb 0.71) to point toward the understandable discrepancy in the metal contents of waste ashes based on the locations, characteristics of the feed waste material, and to some extent on the operating conditions.

3.2 Chelant-assisted washing treatment of waste ashes

3.2.1 Effect of chelant application

The APC-assisted washing of the metal-laden solid waste materials, in combination with the mechanochemical processes, is one of the few enduring treatment alternatives to reclaim or confine the metals (Dermont et al. 2008, Hasegawa et al. 2013a, Hasegawa et al. 2013c). The APCs are capable of creating stable and water-soluble metal complexes, and the EDTA has most often been utilized due to the comparative superior competency among the APCs (Leštan et al. 2008). The EDTA-induced washing yield (%) of the rare metals, with content above 50 mg kg^{-1}, in four representative waste samples of each ash type (IFA, MFA, TPP-FA, or MMA) is shown in Figure 2.

In a neutral pH environment and at a room-temperature condition (25±2 °C), the EDTA (0.01 mol L^{-1}) has shown better extractability than the control experiments performed using ultrapure water as expected in most cases. The extracted contents of some rare metals, such as Mn, Ni, In, Sb, Ti, and Te, have been either very negligible or below the detectable limit with EDTA and the ultrapure water irrespective of the ash types. The extraction of few metals has been achieved from certain ash types only, e.g., B was available from TPP-FA and MMA and remained confined in the IFA or MFA. The overall rate of extraction achieved with chelant application cannot be defined as promising though. The metals in the ash particles may exist in the form of oxide, carbonate, chloride, and sulfate, while the oxide form predominates (Verhulst et al. 1995). The lower rate of extraction achieved with chelant application is thus attributable to the decreasing tendency in the solubility of oxides and other solid phases at the neutral conditions because of the formation of metal-hydroxy complexes (Elliott & Brown 1989).

3.2.2 Effect of chelant types and corresponding metal-chelant stability constants

The lower biodegradability of EDTA evokes environmental concern (Nowack & VanBriesen 2005), and, hence, eco-friendly biodegradable chelants are preferred as a replacement of EDTA for the treatment of metal-contaminated solids. In the current work, we

have used two biodegradable chelants, EDDS and HIDS, and the comparative performances have been illustrated in Figure 2. A better recovery with EDTA than that with the biodegradable chelants was accomplished in several cases, whereas there also have been occasional exceptions (W: EDDS, IFA, and MFA; B: HIDS, TPP-FA, and MMA; Sb: HIDS, MFA, and MMA; Li: HIDS, TPP-FA; V: HIDS, TPP-FA). The comparative decrease in the extraction ability among the chelants can be correlated to the corresponding stability of the respective metal-chelant complexes ($\log K_{ML}$) in solution, which depend on the total number of donor atoms and coordinating sites, and types of the donor atoms in the chelant (Martell & Hancock 1996). The stability information of the metal-chelant complexes with EDTA and EDDS have been extracted from the "NIST Critically Selected Stability Constants of Metal Complexes Database" (Martell et al. 2004) and compiled in the Table 1, while the relevant information for HIDS is not available in the literature. The extraction yield of Sr metal with EDTA (IFA 25.1, MFA 30.4, TPP-FA 5.5) and EDDS (IFA 21, MFA 21.6, TPP-FA 0.3) followed the comparative order of $\log K_{ML}$ (EDTA 8.72, EDDS 3.7). The instance of Sr metal can be used as an example of the predicted correlation between the extraction yield and corresponding $\log K_{ML}$ values. However, the correlation might not be sustained if the extraction process has been influenced by other interrelated factors, such as changes in the acidity, changes in solution ionic strength, or changes in the redox potential (Pickering 1986, Begum et al. 2013).

3.2.3 Effect of chelant concentrations

The incineration fly ashes are reported to contain a remarkably higher amount of Cl, Ca, K and Na compared to the other elements, which makes up approximately 60% of the total elements in the fly ashes and remains in the form of soluble salt (Hong et al. 2000, Jung & Osako 2009). The APCs are nonselective toward metals, and the chelant-assisted extraction yield of the target metal species has often been hindered or reduced to a considerable extent due to the presence of competitive ionic species at a higher concentration (Begum et al. 2012a, Begum et al. 2013). Therefore, the application of varying EDTA concentrations has

been evaluated with the postulation that a higher chelant concentration may increase the extraction capability. The findings are illustrated in Figure 3, which shows a gradual increase in the extraction yield (%) with the higher chelant concentration in solution. The changes have been frequently remarkable with 0.10 mol L^{-1} chelant compared to those of 0.01 mol L^{-1}.

3.2.4 Effect of temperature conditions

The affirmative impact of temperature conditions during the extraction of metals with chelants has been witnessed during the reclamation of indium from the waste liquid-crystal display panels (Hasegawa et al. 2013a, Hasegawa et al. 2013c). An intensified temperature environment in the range of 40 to 98 °C with an approximate interval of 20 °C has been used to test the comparative extraction yield, and the results showed that the conditions above room temperatures cause a higher metal leaching with chelants (Figure 4). There is a possibility of chelant degradation at higher temperatures (Hasegawa et al. 2013a). A better extraction can be achieved even in the range of 60 to 80 °C and, hence, is recommended to avoid any loss in chelant due to the boiling effect or degradation.

3.2.5 Mechanochemical effect of ultrasound irradiation

The incorporation of the metals within the solid phase of the ash particles might be one of the factors other than the extractant concentration, coexisting ion concentrations, or comparative selectivity of the chelants toward the metal ions, which controls the release of metals from the ash (Peters 1999, Begum et al. 2013). The metals partitioned within the crystalline lattice of the solid particles are unlikely to be extracted easily with the extractants (Barona et al. 2001). The destruction of the crystalline structure within the solid phase can be done with the aid of the mechanochemical treatment, which could facilitate the increased metal dissolution with the chelants (Hasegawa et al. 2013c). In recent years, the use of US in leaching processes is becoming increasingly popular in hydrometallurgy, and the competence of US irradiation as a mechanochemical force to intensify the metal-leaching in acid-assisted processes or with other solvents except that of the chelant have been reported (Swamy &

Narayana 2001, Öncel et al. 2005, Beşe 2007, Elik 2007, Shen et al. 2013). In the current work, the chelant-assisted extraction yield (%) with the US irradiation and usual shaking treatment has been tested, and a significant impact of the US irradiation on the metal extraction has been observed (Figure 5). The rate of mobility toward solution is increased outstandingly for almost all the metals with the chelant concentration of 0.01 mol L^{-1} and at room temperature (25 ± 0.5 °C).

4.0 Conclusion

The work reports the possibility of waste ash recycling as a secondary resource for the 30 depleting metals that are important to formulate clean energy devices, as well as proposed an approach for reclamation. The ash varieties, abbreviated as IFA, MFA, TPP-FA, and MMA, represent different waste origins, and the characteristics of the feed-waste noticeably influence the content of rare metals in each of the ash types. The fluctuation in the rare metal concentrations within each of the ash types has been perceived with the observations that only nine metal species persist at a maximum of 50 mg kg^{-1} concentration. The chelant-assisted reclamation of the rare metals has been checked using the following APCs: EDTA, EDDS, and HIDS, and the latter two of the APCs possess biodegradable characteristics and evaluated as the alternative to EDTA. The extraction yields with the EDTA remain superior (chelant concentration 0.01 mol L^{-1}; pH 7) than those with the EDDS or HIDS, which can be explained using the comparative metal-chelant stability constants. Higher chelant concentration in solution (0.05, 0.10, and 0.15 mol L^{-1}), increased system temperature (40, 60, 80, and 98 °C), and US irradiation have been verified to improve the extraction yield. A chelant concentration of 0.10 mol L^{-1} or an increase of the system temperature within the array of 60 to 80 °C can increase the extraction yield favorably. The application of the US irradiation created the most substantial enhancement in the extraction performance of APCs. A better dissolution of the rare metals with the chelant-loaded washing solution at minimum chelant concentration and at room-temperature has been achieved due to the mechanochemical energy created via the US irradiation.

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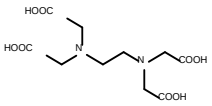
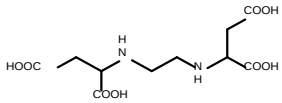
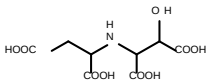
Table 1: Chemical structure, acid dissociation constants (pK_a) of the chelants, and initial speciation of chelant in the assay mixture (at pH 7; 1:1 molar ratio), and stability constants of metal-chelant complexes

APCs	Structure	pK_a				Speciation of chelant in the assay mixture (% of total chelant) [c]
		pK_{a1}	pK_{a2}	pK_{a3}	pK_{a4}	
EDTA [a]		2.00	2.69	6.13	10.37	$HEDTA^{3-}$ (87.7), H_2EDTA^{2-} (12.0)
EDDS [a]		2.95	3.86	6.84	10.01	$HEDDS^{3-}$ (58.9), H_2EDDS^{2-} (41.1)
HIDS [b]		2.14	3.08	4.07	9.61	$HHIDS^{3-}$ (99.5)

Stability constants ($\log K_{ML}$) of metal-chelant complexes [a]

Metal	$\log K_{ML}$		Metal	$\log K_{ML}$		Metal	$\log K_{ML}$	
	EDTA	EDDS		EDTA	EDDS		EDTA	EDDS
B	–	–	Lu	19.74	14.32	Sr	8.72	3.7
Ce	15.93	12.67	Mn	13.89	8.75	Ta	–	–
Co	16.45	14	Nb	–	–	Tb	17.87	13.51
Dy	18.3	13.59	Nd	16.51	13.03	Te	–	–
Eu	17.25	13.54	Ni	18.4	16.7	Ti	21.3	0
Ga	21.7	–	Pr	16.3	12.96	Tm	19.32	14
Gd	17.35	13.45	Rb	0.6	–	V	12.7 [d]	–
Hf	–	–	Sb	12.46 [d]	–	W	–	–
In	25	22	Se	–	–	Y	18.08	13.55
Li	2.95	–	Sm	17.06	13.46	Yb	19.49	14.13

[a] At 25 °C (μ = 0.1 M) (Martell et al. 2004).
[b] At 25 °C (μ = 0.1 M) (Begum et al. 2012c, Begum et al. 2012b).
[c] The major species of chelants exist in the assay mixture is listed only, and the other species is excluded when the % formation of the dominant species is > 99.5. The calculations have been performed using the computer program HySS2009 (Alderighi et al. 1999).
[d] At 20 °C (μ = 0.1 M) (Martell et al. 2004).

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Table 2: The rare metal contents (mg kg^{-1}) in the waste ashes (n = 3), and comparison with the crude ore quality and concentration in the earth crust.

Metal	IFA [a]									MFA [a]				TPP-FA [a]					MMA [a]	COQ [b]	COC [b]
	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-11	S-12	S-13	S-14	S-15	S-16	S-17	S-18	S-19		
B	212±42	190±18	189±3	196±22	168±15	203±7	220±6	400±11	541±16	275±9	289±7	380±9	71±5	151±5	100±1	144±9	353±15	622±23	87±1	–	10
Ce	10±0.3	16±2	8±1	10±1	14±1	8±0.2	18±1	8±0.3	9±0.5	–	–	–	–	91±4	35±1	59±3	51±0.4	7±0.2	0	–	33
Co	–	–	–	–	–	–	–	–	–	–	–	–	–	–	76±1	–	–	–	–	2300	29
Dy	–	–	–	–	–	–	–	–	–	–	–	–	–	11±0.3	8±0.2	9±0.2	1±0.1	–	–	–	3.7
Eu	2±0.02	2±0.1	1±0.1	1±0	1±0.1	1±0.02	1±0.02	1±0.02	1±0.01	–	–	–	–	2±0.1	2±0.1	2±0.03	1±0.1	–	–	–	1.1
Ga	-	4±0.3	4±1	11±0.2	3±0.2	10±1	8±0.1	10±1	10±1	96±6	17±0.4	9±3	15±1	49±1	41±1	33±1	17±1	5±0.3	8±0.4	–	18
Gd	26±1.2	26±2	21±3	11±0.3	23±1	17±0.4	21±1	17±1	20±1	4±0.4	0	8±1	0	34±1	42±0.2	24±1	26±2	56±2	0	–	3.3
Hf	–	–	–	–	–	–	–	–	–	–	–	–	8±0.6	–	–	–	–	–	–	–	3
In	–	–	–	–	–	–	–	–	–	2±0.3	–	–	–	–	–	–	–	–	23534±118	10	0.05
Li	40±1.3	55±6	61±4	89±3	47±2	108±4	80±4	68±2	110±4	34±1	35±1	58±3	77±4	187±3	167±5	94±2	142±1	56±1	9±0.3	1400	13
Lu	1±0.03	1±0	1±0.1	–	1±0.02	–	–	–	1±0.02	–	1±0.2	–	–	2±0.1	2±0.02	2±0.04	2±0.1	1±0.03	–	–	0.3
Mn	1345±41	588±36	480±42	537±9	612±2	521±3	558±6	424±3	539±4	368±12	490±5	609±12	280±9	275±4	72±0.3	141±3	629±1	664±10	14±0.3	250000	1400
Nb	15±1	16±1	14±2	23±1	16±1	12±0.3	15±1	12±1	13±0.3	–	–	10±0.2	–	41±1	53±0.4	33±1	24±1	33±1	–	1400	11
Nd	–	–	–	–	–	–	7±0.3	–	–	–	–	–	–	43±2	18±1	29±1	13±1	–	–	–	16
Ni	69±7	140±15	247±13	47±2	214±8	111±1	77±2	50±3	80±4	8±1	170±7	94±4	20±3	57±1	155±2	55±1	115±1	148±3	7±0.4	10200	105
Pr	–	–	–	–	–	–	–	–	–	–	–	–	–	12±1	1±0.01	8±0.3	7±1	–	–	–	3.9
Rb	124±3	146±4	143±1	186±6	120±1	183±2	174±3	163±7	174±4	1221±15	1120±15	811±18	1119±12	134±3	118±5	137±4	166±1	117±1	113±3	–	–
Sb	274±10	557±17	895±62	1454±25	310±7	1222±3	1049±9	612±8	2107±38	255±9	836±24	828±24	545±23	1±0.3	1±0.03	1±0.1	–	1406±31	242±14	9900	0.2
Se	1±0.2	1±0	1±0.2	4±0.1	1±0.01	3±0.2	3±0.4	2±0.1	3±0.1	3±0.3	19±4	2±0.5	20±1	3±0.2	2±0.1	2±0.3	2±1	–	2997±53	2000	0.05
Sm	-	-	-	1±0.1	0	1±0.1	0	1±0.2	0	17±0.4	5±0.6	22±3	1±0.5	10±1	3±0.5	7±0.4	–	–	–	–	3.5
Sr	262±6	244±17	216±12	189±5	234±2	192±1	224±2	212±6	253±1	63±2	191±7	435±19	475±24	946±16	347±5	549±12	587±2	284±7	3±0.1	–	260
Ta	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	170	1
Tb	2±0.2	2±0.2	1±0.1	2±0.2	2±0.1	2±0.2	1±0.1	1±0.1	2±0.2	5±0.4	10±1	8±1	6±0.4	3±0.2	2±0.03	2±0.03	2±0.1	0	1±0.01	–	0.6
Te	5±0.4	5±0.4	5±1	2±0.4	128±2	5±0.1	6±0.7	5±0.4	10±0.3	10±1	4±1	1±0.5	–	–	–	–	–	13±1	2616±126	–	0.02
Ti	8536±181	9329±21	9004±127	5296±119	8155±82	7300±11	8691±9	7489±112	7826±89	383±7	3299±13	15380±155	152±8	5766±51	10577±92	4060±34	3956±22	–	5±0.5	310000	5400
Tm	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	0.32
V	21±1	21±1	19±2	28±1	22±1	18±0.3	18±1	16±1	17±1	47±3	52±3	48±3	32±2	179±4	296±3	156±3	132±1	26±1	0	1400	230
W	218±13	225±16	270±21	443±8	144±3	518±2	326±1	354±8	629±14	2781±14	1607±19	517±16	1334±17	12±0.4	14±2	10±1	13±0.3	99±1	1410±56	12000	1
Y	10±2	13±2	8±1	11±0.3	11±0.3	13±1	14±1	10±0.4	12±1	1±0.3	5±0.1	7±1	4±0.3	64±2	41±1	51±2	25±2	1±0.04	–	–	20
Yb	1±0.01	1±0.1	–	1±0.01	2±0.2	1±0.02	1±0.01	–	1±0.02	–	1±0.2	1±0.2	1±0.2	9±0.2	7±0.04	7±0.2	4±0.3	1±0.03	–	–	2.2

'–'stands for 'Below Detection Limit' or 'Data Not Available'. [a] *IFA* Incineration Fly Ash, *MFA* Molten Fly Ash, *TPP-FA* Thermal Power Plant Fly Ash, *MMA* Non-Ferrous Metal Processing Plant Ash.
[b] COQ: Crude Ore Quality (mg kg^{-1}) ; COC: Concentration in the crust (mg kg^{-1}); Data extracted from Halada et al. (Halada et al. 2001).

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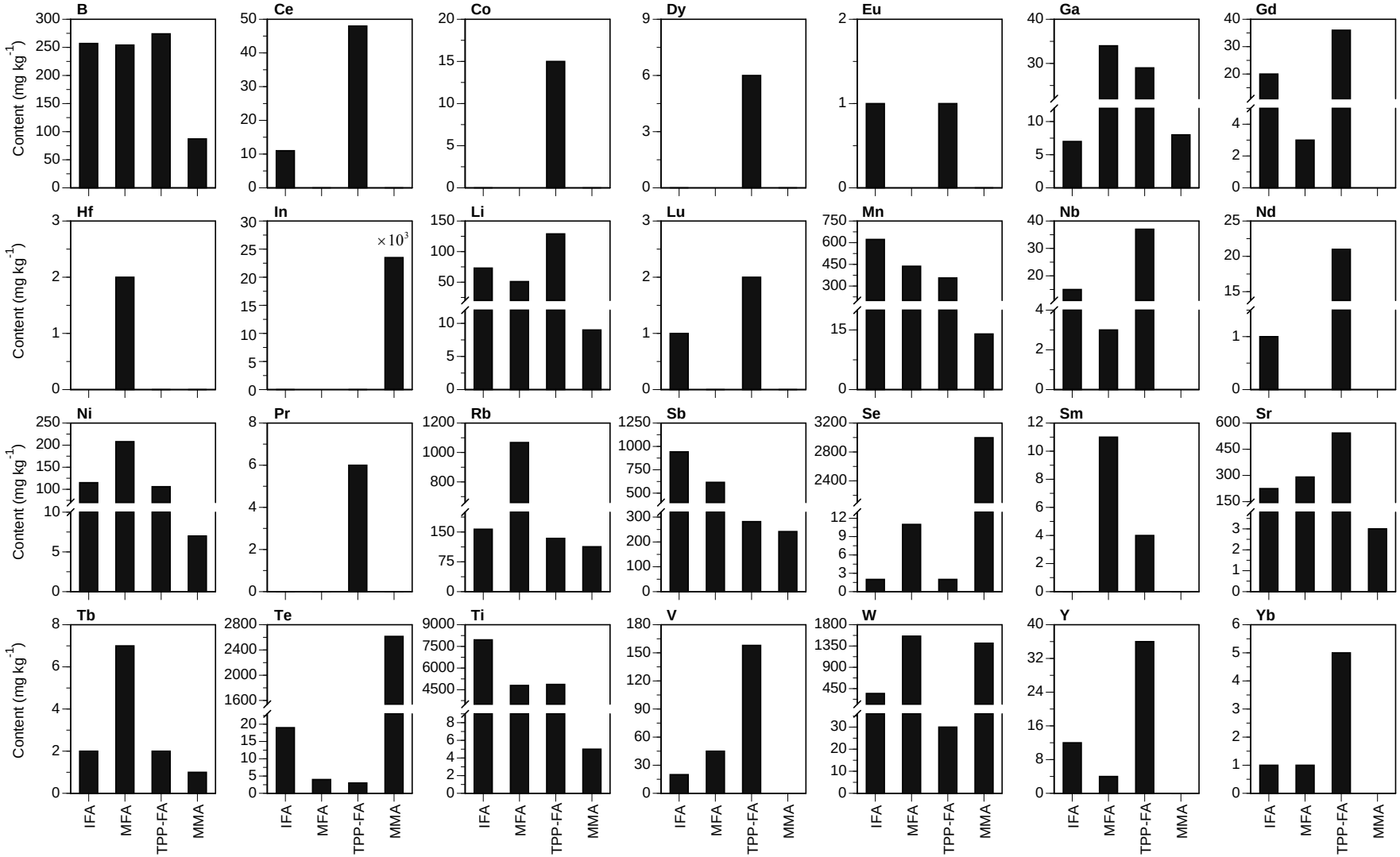

Figure 1: Comparative availability of rare metals in different waste ash types (*IFA* Incineration Fly Ash, *MFA* Molten Fly Ash, *TPP-FA* Thermal Power Plant Fly Ash, *MMA* Non-Ferrous Metal Processing Plant Ash).

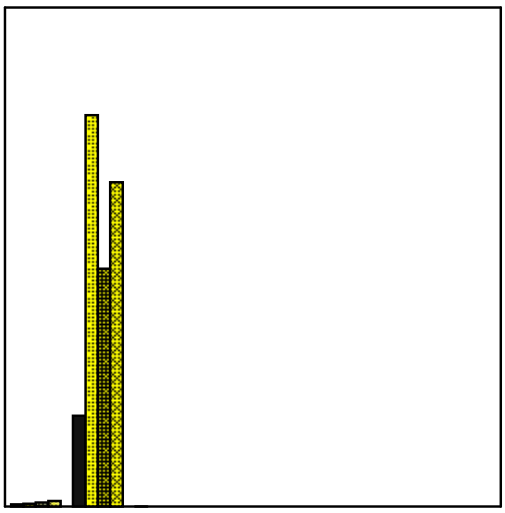

Figure 2: Chelant-assisted extraction yield of rare metals from the different waste ash types with different chelants (EDTA, EDDS, and HIDS) (*IFA* Incineration Fly Ash, S-6; *MFA* Molten Fly Ash, S-11; *TPP-FA* Thermal Power Plant Fly Ash, S-17; *MMA* Non-Ferrous Metal Processing Plant Ash, S-19; chelant concentration, 0.01 mol L^{-1}; pH 7; temperature, 25 ± 2 °C; $n = 3$).

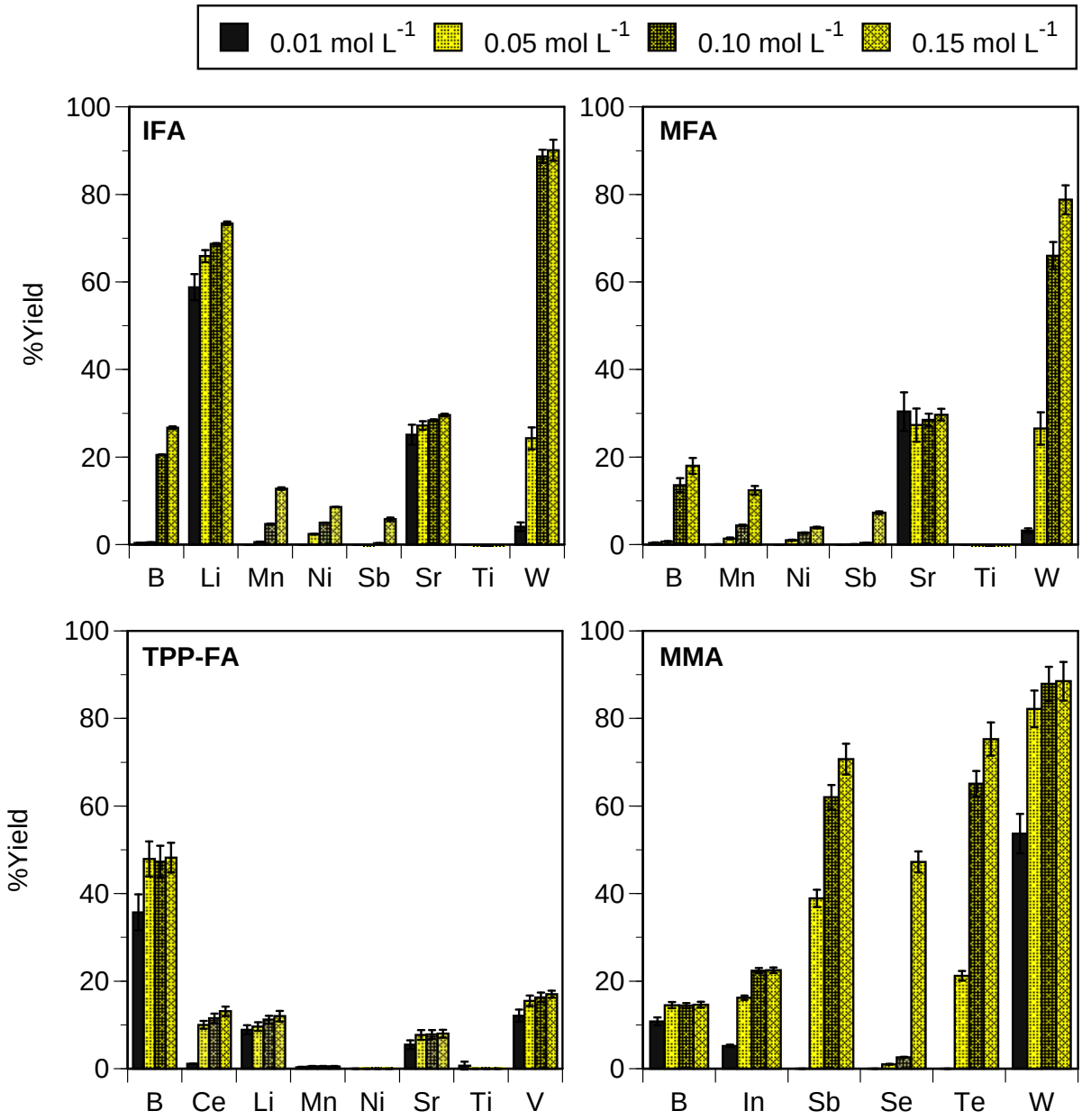

Figure 3: Effect of chelant concentration on the extraction yield of rare metals from the different waste ash types (*IFA* Incineration Fly Ash, S-6; *MFA* Molten Fly Ash, S-11; *TPP-FA* Thermal Power Plant Fly Ash, S-17; *MMA* Non-Ferrous Metal Processing Plant Ash, S-19; chelant, EDTA; pH 7; temperature, 25 °C; $n = 3$).

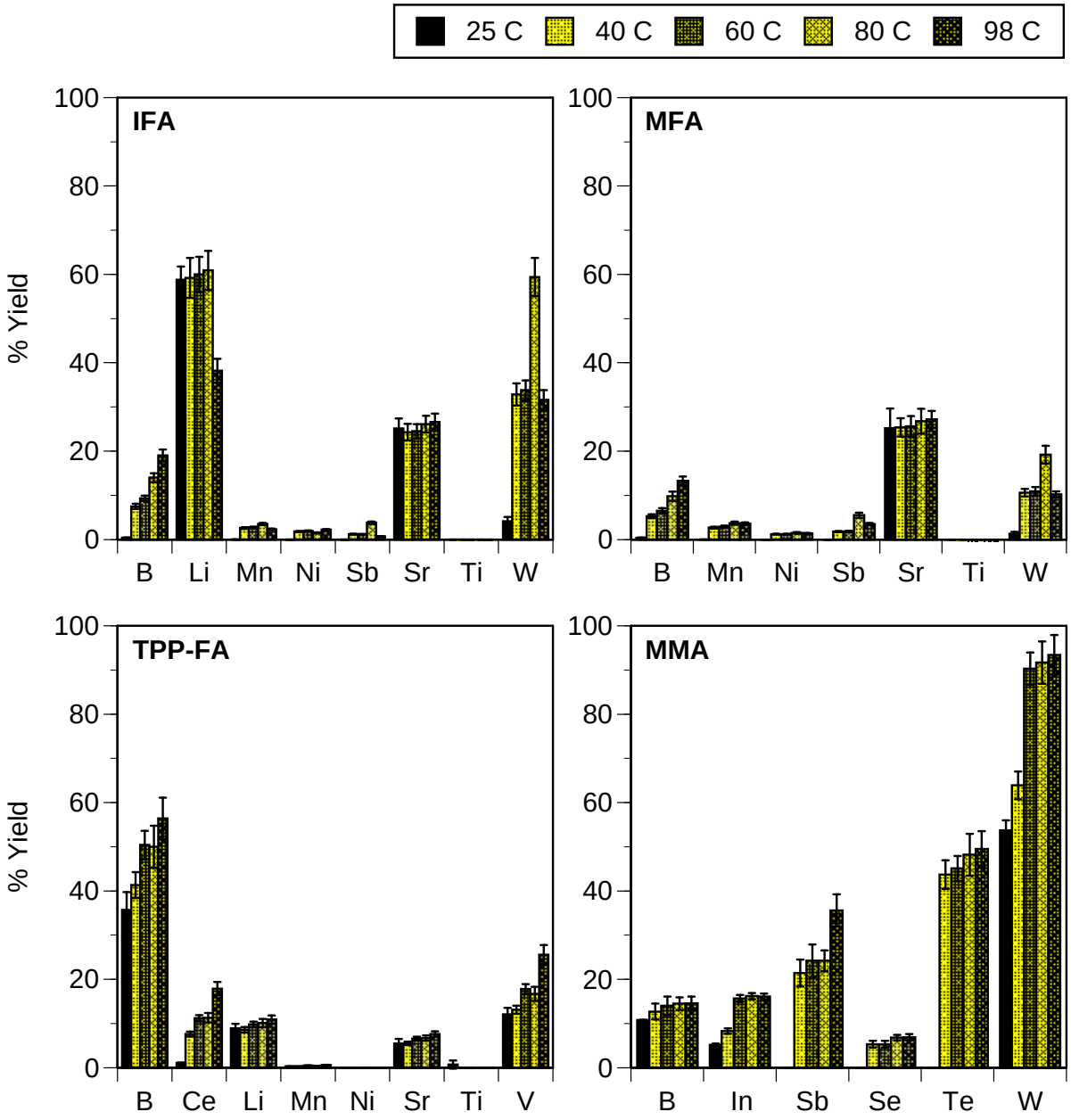

Figure 4: Effect of varying temperature conditions on the extraction yield of rare metals from the different waste ash types (*IFA* Incineration Fly Ash, S-6; *MFA* Molten Fly Ash, S-11; *TPP-FA* Thermal Power Plant Fly Ash, S-17; *MMA* Non-Ferrous Metal Processing Plant Ash, S-19; chelant, EDTA; chelant concentration, 0.01 mol L^{-1}; pH 7; temperature, 25 °C; $n = 3$).

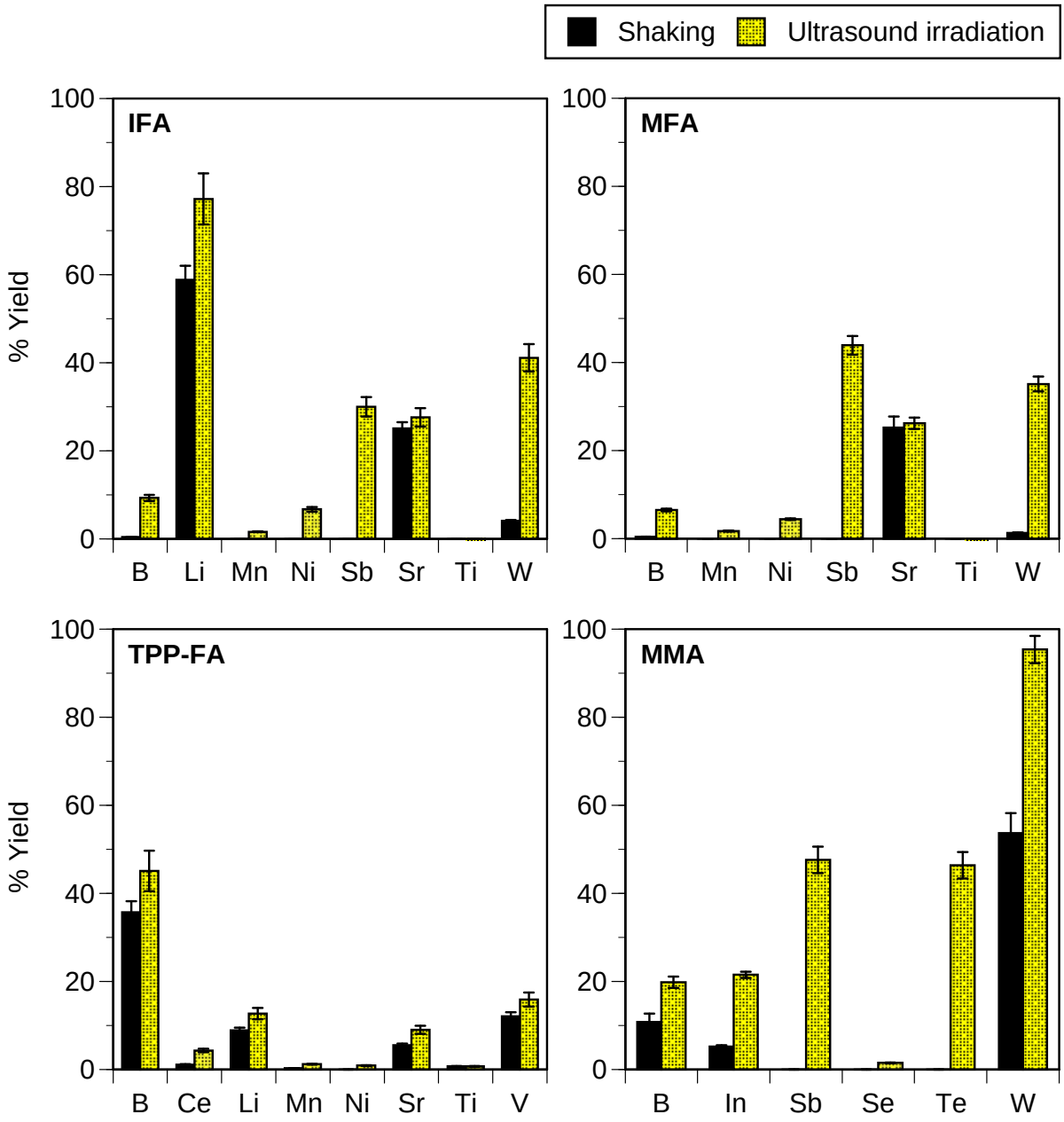

Figure 5: Effect of ultrasound irradiation on the extraction yield of rare metals from the different waste ash types (*IFA* Incineration Fly Ash, S-6; *MFA* Molten Fly Ash, S-11; *TPP-FA* Thermal Power Plant Fly Ash, S-17; *MMA* Non-Ferrous Metal Processing Plant Ash, S-19; chelant, EDTA; chelant concentration, 0.01 mol L^{-1}; pH 7; temperature, 25 °C; $n = 3$).