

# An Overview of Rare Earth Elements in Sewage Sludges and Their Ashes <sup>†</sup>

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**Abstract:** In this work, data about REY concentrations in sewage sludges and their ashes have been analysed. The source of REY in them is mainly geogenic, which is why sludges from regions like China and Brazil have higher concentrations. Thus, the combustion or co-combustion of sewage sludge as a way of recovery its energy potential and, secondarily, the processing of their ashes in order to obtain REY may be interesting, in certain regions, depending on the techno-economic and environmental context of the moment.

**Keywords:** sewage sludge; rare earth elements; ashes; earth's crust

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## 1. Introduction

Both the adequate management and valorisation of sewage sludge are crucial for achieving a zero-waste scenario and, consequently, for promoting the circular economy and ensuring sustainability. Its valorisation should not only imply the recovery of its energy potential, but also of its nutrients (N and P), and those valuable metals with significant concentrations [1].

Although there are scarce published data about the concentrations of rare earth elements (lanthanides) plus scandium (Sc) and yttrium (Y) (REY) in sewage sludges and their ashes [1–10], data show that sludges contain REY. There is no consensus about the interest of recovering REY from sewage sludge and its ashes. Some authors [11] think that REY may be recovered from sewage sludge ashes, whilst others [1] assert that these elements show little enrichment in sludges, which makes its recovery non-interesting.

The objective of this work is to deepen in the knowledge of the feasibility of sewage sludge and its ashes as a source of REY. Thus, an overview of the REY contents in these materials was performed. These data plus our own data about REY concentrations in sewage sludges from three urban wastewater treatment plants (WWTPs) sited in Asturias (Spain) were used to acquire a better knowledge of REY availability. Moreover, relationships between REY concentrations in sludge ashes and those of major and minor elements were also studied.

## 2. Materials, Methods and Data Used

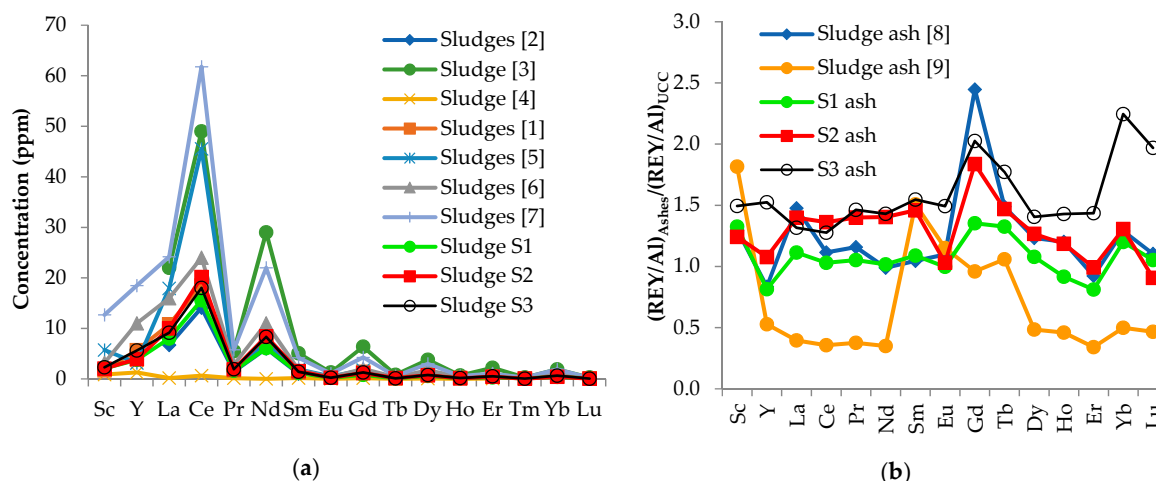
Some data used in this paper were obtained from (1) published articles and (2) new data from our own analysis. The sludges are from Japan [2,3], the USA [1,4], Switzerland [5], Sweden [6], China [7] and Spain (new data). The Japanese sludges came from 14 different wastewater treatment plants (WWTPs) [2], whilst the one studied by Gao et al. [3] come from an industrial WWTP. Vriens et al. [5] analysed sludges from 64 municipal and industrial WWTP located in Switzerland. On the other hand, Verplanck et al. [4] and Westerhoff et al. [1] studied sewage sludges from several plants sited in the USA, 1 and 96 WWTPs, respectively. The Swedish sludges come from 48 urban WWTP [6], while Zhang et al. [7] analysed 33 samples from sewage discharge channels of one of the largest cities in China (Tianjin), which has several industries. Moreover, REY concentrations of three more sewage sludges (S1, S2 and S3) from different WWTPs of Asturias (Spain) were added.

Regarding to the sludge ashes, few articles [8–10] report the concentrations of REY in them. Those considered in this work come from Germany [8], Japan [9], and Spain (from S1, S2 and S3). The sludge ashes from Germany [8] were produced in 26 incineration facilities, from which 15 burn solely municipal sewage sludge, 3 solely industrial sludge and 8 a mixture of both. The ashes used by Zhang et al. [9] were obtained from one sewage sludge of Japan at similar conditions of an incineration plant (850 °C during five hours). Finally, our ashes were obtained in an electric laboratory furnace under a dynamic air atmosphere. The samples were heated at 10 °C/min up to 1100 °C and, then, this temperature was maintained during one hour. Previously, the sludges had been dried at 105 °C and ground at a size lower than 200 µm. REY in the ashes and sludges were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) and ICP-atomic emission spectrometry (ICP-AES) after samples acid digestion with HClO<sub>4</sub>-HNO<sub>3</sub>-HCl-HF.

## 3. Results and Discussion

### 3.1. REY Concentrations in the Sludges

Figure 1a shows the mean REY concentrations of the sludges from several authors' research [1–7] and those of the sewage sludges from Spain.



**Figure 1.** REY in the sludges and their ashes: (a) Concentrations in the sludges; (b) Enrichment factors relative to Al (EFs) of sludge ashes.

REY concentrations show approximately the same pattern, independently of the country of origin (Figure 1a). Also, in general, they are lower than those of the upper continental crust (UCC) [12], excepting for Sc, Eu, Gd, Tb and Yb in the Chinese sludges [7] and Nd, Eu, Gd, Dy and Ho for the industrial sludge [3], whose concentrations are at least 10% higher than those of the UCC.

The highest relative concentrations compared to those in the UCC are reached for Sc in the Chinese sludge [7] and Gd for the industrial sludge [3]. These relative concentrations (REY concentration in the sludge/REY concentration in the UCC) are 1.8 and 2.3, respectively. Verplanck et al. [4] found large enrichments in Gd compared to other REY in the influent and effluent waters of various WWTPs, but only in one sludge sample of 17 analysed. This is in good agreement with the fact that the Chinese sludges come from sewage discharge channels [7]. On the other hand, Gd may have mainly an anthropogenic source, since it is used as a contrasting agent in magnetic resonance imaging [4]. In general, the REY concentrations in the Chinese sludge [7] are very similar to those of the UCC. This agrees with the fact that China has the highest global REY resources and is the main producer of them [13]. The fact that these concentrations are similar to those of the UCC indicates that their ashes may have significant concentrations of REY, since the sludges have important quantities of organic matter (with a medium value of 15.5% [7]) that is removed during combustion. Folgueras et al. [10] did not find volatilization of REY after sludge combustion at 800 °C and 1100 °C, which may be attributed to their inorganic association. However, some researchers [14] reported partial REY volatilisation after coal combustion in power plants. If REY do not volatilise, for an organic matter content of 15.5%, REY concentrations in the sludge ashes will be 1.2 times higher than those of the sludges.

### 3.2. REY Concentrations in the Sludge Ashes

Figure 1b shows the REY enrichment factors relative to Al (EFs) for the mean concentrations of published sludge ashes [8,9] and those of the sewage sludge ashes from Spain (S1, S2 and S3). The EF is the ratio of the concentration an element relative to Al in the sludge ashes divided by that of the same element in the UCC [1]. Aluminium was chosen as the reference element because it is more likely that its content remains approximately constant, because its source is mainly geogenic [1]. The majority of the values are in the range between 1.5 and 0.5 (Figure 1b). The EFs for La, Ce, Pr, Nd and Er of the Japanese sludge have values around 0.4, whilst Sc of the Japanese sludge, Yb and Lu for S3 and Gd for the German sludge, S2 and S3 have values higher than 1.5, they being 1.8, 2.2, 2.0, 2.5, 1.8 and 2.0, respectively. Therefore, in general, REY concentrations in sludge ashes are relatively similar to those of the UCC, which indicates that the main source of them is earth's crust. Westerhoff et al. [1] pointed out that REY excepting for Gd in sewage sludges from the USA have mainly a crustal origin. Morais et al. [15] analysed some trace elements including Sc, Y, La, Ce and Nd in the ashes of a sewage sludge (obtained after heating at 1050 °C during 3 h) from one of the largest Brazilian WWTPs. For this sludge, EFs of Sc, Y, La, Ce and Nd are 1.9, 1.3, 2.2, 2.3 and 1.3, respectively. These relatively high values in comparison with those of the other sludges may be related with the fact that Brazil has higher resources of REY (11% of the global ones) than Japan, the USA and Europe [13].

For the ashes of the three Spanish and the Japanese [9] sewage sludges together with the mean of the German sludges [8], the concentrations of REY were plotted against those of major and minor elements. Positive relationships were found between Sc, Sm and Eu concentrations and those of P<sub>2</sub>O<sub>5</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>O and, for Sc and Eu with Na<sub>2</sub>O. They were also found for Ce and Pr against TiO<sub>2</sub>. The correlation coefficients were higher than 0.7 in all cases.

The fact that Sc, Sm and Eu concentrations are related to those of various major and minor elements is due to the fact that there are also linear relationships between any two of them (P, Al, Mg and K) and with Na ( $R^2 > 0.7$ ). The EFs of ash major and minor elements range in the intervals 56–270, 1.0–1.7, 0.02–0.5, 0.06–3.7, 0.08–1.9, 2.0–15 and 0.9–9.0 for P, Mg, Na, K, Ti, Ca and Fe expressed as oxides, respectively. The high EFs of P<sub>2</sub>O<sub>5</sub> clearly indicates that it comes from an anthropogenic source, specifically from detergents and fertilisers (both contain phosphates). On the other hand, in some sludges, Ca and Fe have also anthropogenic sources, since, in some WWTPs, Ca(OH)<sub>2</sub> and FeCl<sub>3</sub> are used as sludge additives [10]. The existence of linear positive relationships between P, Al, Mg, K and Na indicates that their concentrations in the sludge ashes increase with the quantity of phosphates in the wastewater. Not only earth's crust but also detergents and fertilizers in the wastewater are a source of REY in the sewage sludges and their ashes. However, the erosion and weathering processes of rocks are likely to be the main responsible for the contents of REY in them,

since their EFs are relatively low, the highest value being 2.5 (Figure 1b). Goodenough et al. [16] stated that, in Europe, the primary deposits of REY are mainly associated with alkaline igneous rocks and carbonatites that contains REY-bearing minerals. Also, the weathering of granitic or igneous rocks can lead to the formation of aluminosilicate clays, such as kaolinite and illite [17]. X-ray diffraction (XRD) of the Spanish sludge ashes obtained at 800 °C has shown the presence of clays and chloroapatite [10]. Thus, REY in sludges may be associated with phosphates and clays.

Although some phosphates and carbonates are sources of REY with relative high concentrations of them, their leaching need aggressive conditions that leads to elevated recovery costs [17]. Sewage sludges and their ashes have much lower concentrations of REY. However, they also have the following advantages compared to the traditional ore minerals and deposits: (1) sewage sludge do not need mining processes, (2) huge quantities of this type of waste are produced every year, (3) sewage sludge has to be properly treated, its valorisation being more desirable, and (4) its leaching is much simpler. According to this, sewage sludge or its ash from areas rich in REY, such as China and Brazil, may be an interesting alternative source of some REY.

**Author Contributions:** All the authors participated in the different stages of the manuscript elaboration.

**Conflicts of Interest:** The authors declare no conflict of interest.

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