



X-ray Diffraction Analysis of Desulfurant Sorbents Prepared by Mixing Calcined Sewage Sludge and CaO in Distilled or Seawater

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Desulfurant sorbents prepared by hydration, in sea or distilled water, of calcined sewage sludge (ash) and CaO at CaO/ash weight ratios of 0.2 or 3 at room temperature or at 90 ° C, were characterized by X-ray diffraction in order to relate the X-ray composition of the sorbents to the preparation process and to the specific surface area of the obtained sorbents. Results show that the main compounds detected in the sludge's ash are the same than those found in bibliography for the calcined sludge. In all the sorbents, independently of the preparation conditions, Ca(OH)₂ was found instead of CaO used as raw material. New and different crystalline products were found in the sorbents depending on the preparation conditions. All the sorbents prepared in seawater contain NaCl in their composition; the specific surface area of the sorbents increased with hydration time and temperature and was lower when seawater was used for hydration.

1. Introduction

Sewage sludge is the waste left behind after cleaning wastewater. This sludge consists of a complex heterogeneous mixture of organic and inorganic compounds according to Metcalf (2002). In recent years, the number of wastewater treatment plants and consequently the production of sewage sludge has increased, being the problem of sewage sludge disposal one of the most complex environmental problems, which must be resolved in accord with the sustainable development principle. In the developed countries, most of the sewage sludge waste is disposed off in landfills, oceans, or via incineration, none of which are exempt from drawbacks as Werther and Ojada (1999) states. In Spain, the common way of management and valorisation of sewage sludge has been the agricultural use. However, due to the legislation in the European Community not all the sewage sludge can be used as fertilizer and a relevant amount of this sludge is incinerated to reduce the volume of waste. According to the current treatments applied to the sludge, the II Wastewater Sewage Sludge National Plan in Spain (EDAR II-PNLD 2007-2015) provides, as one of its objectives, to increase the efficiency in the treatments carried out in the wastewater plants to optimize the recovery of sludge. The energetic valorisation, the reuse and the agricultural use are some valorisation options expressed in this National Plan.

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There is a growing body of literature from Elías (2000) to Murray (2008), that looks at the costs and benefits of using sludge and sludge treatment by products as raw materials in different production processes: as cement additive, road building material or ceramic material. Recently, the option of recycling the sewage sludge in the form of adsorbents or reactive adsorbents has also been considered as Kante et al. (2008) and Smith et al. (2009) state.

The composition of the sewage sludge of a wastewater treatment plant in Santander (Spain) has been previously reported by Fernandez et al. (2008). In a further study, desulfurant sorbents using calcined sludge were prepared and tested being results reported by Fernandez et al.(2009).

In the present work, the ash obtained by calcination of dry sewage sludge and the sorbents prepared with the ash has been studied by X-Ray diffraction with the purpose of identifying the main crystalline components of the ashes and of the sorbents and relate these components and their amounts to the experimental conditions of preparation and to the specific surface area of the sorbents.

2. Experimental Section

Samples of the sewage sludge were taken off from the local municipal wastewater treatment plant and characterized. The residue obtained from the humidity determination (dry sludge) was ignited to constant weight at 550 °C in a Heron HK-11 oven for two hours. The obtained ashes were milled in a mortar and sieved through an 80 µm mesh.

These ashes were used to prepare the desulfurant sorbents. Table 1 summarize the experimental conditions of preparation of the sorbents.

Table 1: Sorbent's Preparation Conditions

Water	Preparation conditions	CaO / ash ratio	Sorbent Identification
Distilled	15 min at room temp	0,2	A
		3	D
Seawater	7 h at 90 °C	0,2	F
	7 h at 90 °C	0,2	H
		3	K

The specific surface area of the ash and of the prepared sorbents was obtained by using the B.E.T. method in a Micromeritics Asap 2000 equipment.

The crystalline components of the ash and of the prepared sorbents were identified by X-Ray diffraction using a Bruker Advance 8 diffractometer with a Cu anode as the X-ray source using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$), connected to a Difrac Plus program. Samples for X-Ray study were prepared by manual milling in a mortar of agate and placed on the sampler. The diffraction figures of the calcined sludge or of the sorbents were compared to the pattern of all the possible crystalline components of the ashes or of the sorbents.

3. Results and discussion

Table 2 shows the specific surface area values of the sorbents and of the raw materials is presented. Results of Table 2 show that the specific surface area of the sorbents decreases as the amount of CaO used to prepare the solid increases (sorbents A and D or H and K); for the same raw material ratio (sorbents A and F), the specific surface area increases with the temperature and hydration time. Comparing sorbent prepared in distilled or seawater, (sorbents F and H), results show that the sorbents prepared in seawater have slightly lower specific surface area values, probably due to the presence of sea salts that can produce pore plugging.

Table 2: Specific surface area of the sorbents and of the raw materials.

Sorbent Identification	Specific surface area (m ² /g)
A	23.0
D	12.0
F	32.4
H	30.5
K	16.4
Sludge ash	18.3
CaO	3.0

The X-Ray study of the calcined sludge and of the sorbents was performed to know the crystalline compounds present in the solids to relate the preparation variables, raw materials ratio, type of water or temperature and hydration time to the final crystalline structure of the sorbents.

The presence of crystalline compounds more frequently found in the calcined sludge or in the prepared sorbents was investigated.

Figure 1 shows the XRD pattern of the calcined sludge with the diffraction pattern of the more frequent crystalline compounds overlapped. Main diffraction angles of these compounds are referred in the Figure. The figure shows that these four compounds are present in the calcined sludge (ash). These are the most frequent products found in calcined sludge according to bibliography data. Izquierdo et al. (2002). The CaCO₃ is present in high amounts due, in part, to the addition of Ca(OH)₂ in the presence of CO₂ in the plant treatment.

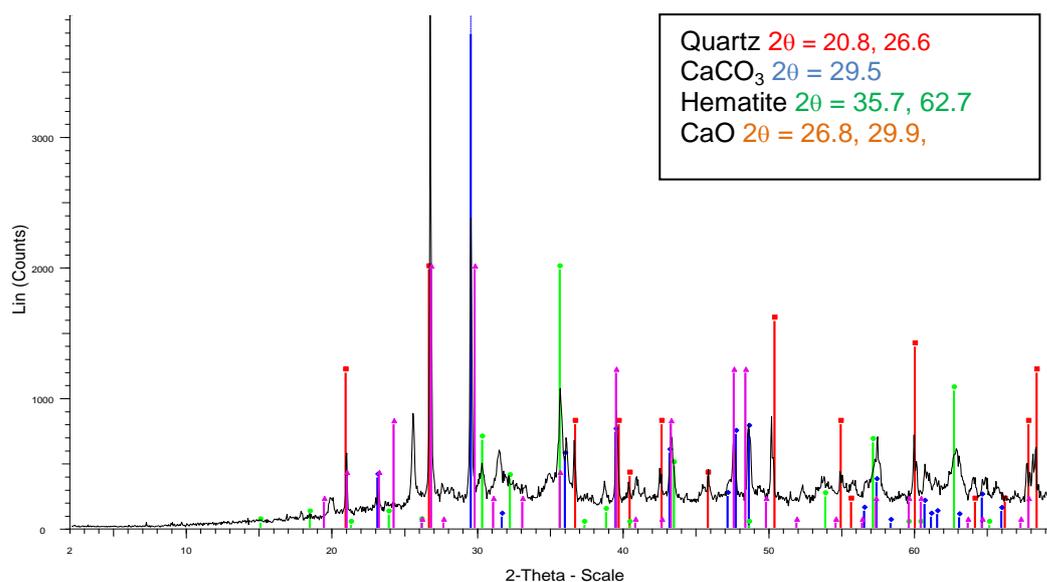


Figure1. XRD of calcined sludge

Next Figures correspond to the XRD patterns of some of the studied sorbents. Figure 2 shows the diffraction figure of the sorbent A prepared, as Table I shows, at a 0.2 CaO / ash ratio, 15 minutes of hydration time at room temperature in distilled water and dried in the oven to constant weight.

In Figure 2, it can be seen that calcium hydroxide is present in the sorbent. This compound has not been found in the calcined sludge; its presence is due to the hydration of the CaO during the preparation of the sorbent. Ca(OH)₂ has been detected in all the sorbents studied independently of the

amount of CaO used in the preparation. Others crystalline compounds detected in this sorbent were quartz, CaCO_3 or Hematite.

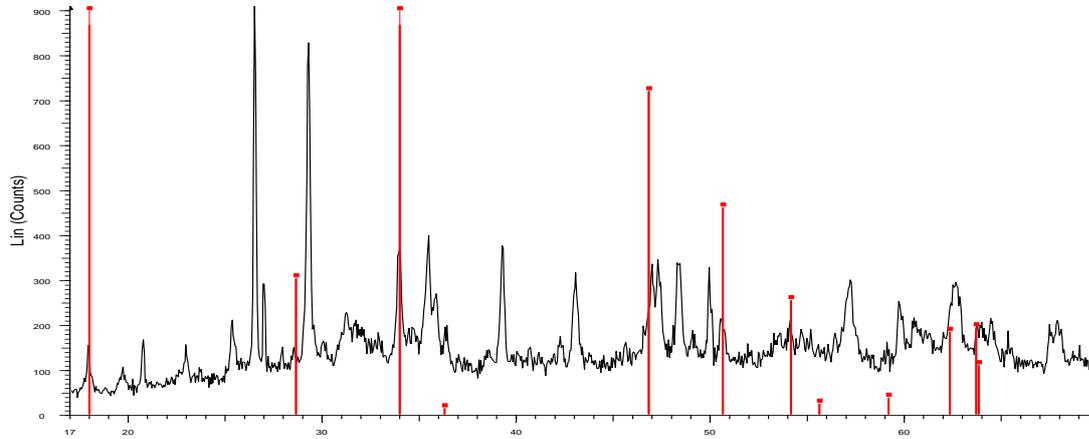


Figure 2. Diffraction figure of sorbent A with the diffraction pattern of Ca(OH)_2 overlapped

Figure 3 shows the diffraction pattern of sorbent D prepared as sorbent A but with a CaO /ash ratio of 3. As figure shows, the intensity of Ca(OH)_2 peaks make difficult the identification of others crystalline compounds also present in the sorbent.

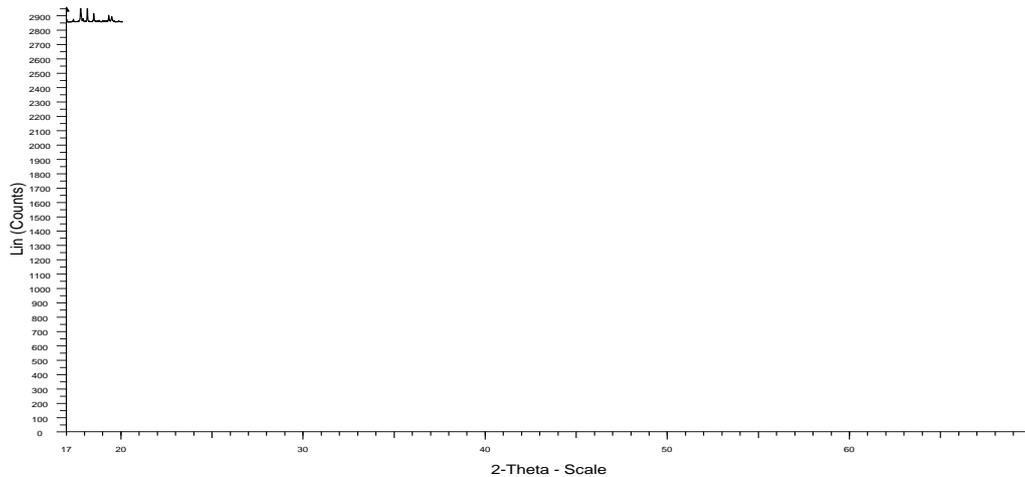


Figure 3. XRD figure of sorbent D

Sorbent F, was prepared at a raw materials ratio of 0.2 as sorbent A, but hydrated for 7 hours at 90°C . Its diffraction figure presents a similar profile than sorbent A; the most relevant difference is the lower intensity of peaks corresponding to Ca(OH)_2 indicating that, as the preparation time and temperature increases, the raw materials react each other to form new products that can explain the increase in the specific surface area value found in sorbent F ($32.4\text{ m}^2/\text{g}$) respect to the surface area of sorbent A ($23\text{ m}^2/\text{g}$). Figure 4 shows a detailed comparison of diffraction figures of sorbents A and F.

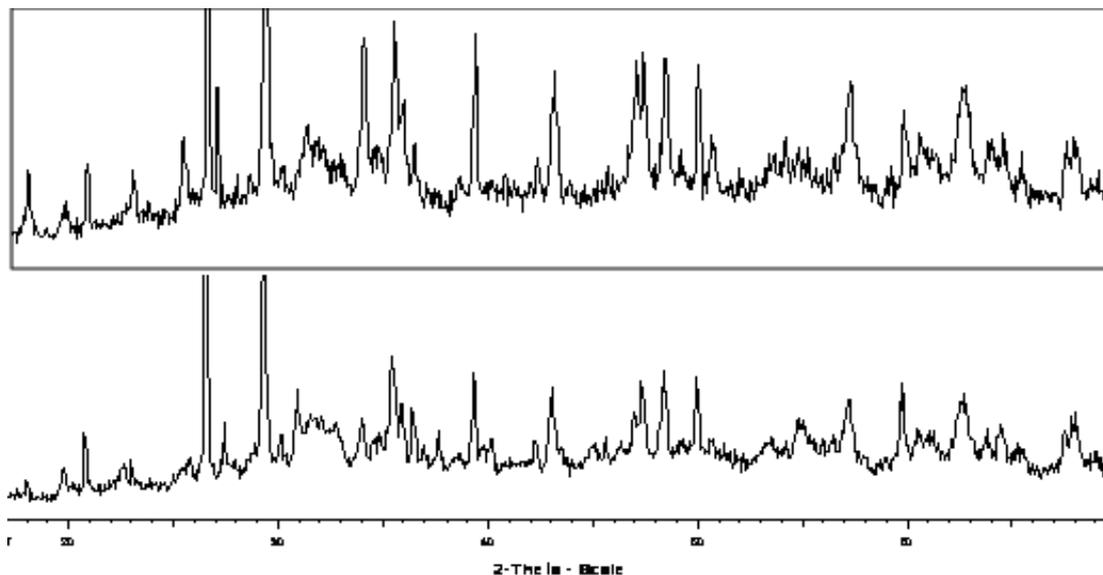


Figure 4. Detail of diffraction figures of sorbents A (up) and F (down)

In the Figure, it can be seen that at 2θ values of 34, 47 and 51 the intensity of the peaks are lower for sorbent F being higher the intensity of peaks at $2\theta = 37.5, 54$ and 55 . These differences are probably related to the generation of new products by reaction between raw materials.

Sorbent H was prepared as sorbent F (0.2 raw materials ratio, 7 hours at $90\text{ }^{\circ}\text{C}$) but in seawater. In this sorbent, it is clearly present the compound Halite (NaCl) the most abundant salt in the seawater. It was also identify quartz, CaCO_3 , hematite and $\text{Ca}(\text{OH})_2$. This last compound is present in higher amount than in sorbent F. This means that the hydration in seawater do not increases the reaction rate between raw materials; this fact can explain the slight lower value of specific surface area of sorbent H ($30.5\text{ m}^2/\text{g}$) respect to sorbent F ($32.4\text{ m}^2/\text{g}$). Figure 5 shows the diffraction figure of sorbent H with the diffraction pattern of NaCl overlapped.

Sorbent K was prepared also in seawater as sorbent H at a 3 CaO / ash ratio. Its XRD figure shows, as sorbent D, the peaks corresponding to $\text{Ca}(\text{OH})_2$ very intense making difficult the identification of the rest of compounds. Because of that its diffraction figure is omitted.

Results of this study allow concluding that the XRD is a good technique to understand the evolution of raw material in the process of preparation of desulfurant sorbents. This evolution allows us to explain the different values of the specific surface area of the sorbents. The study will also help to understand the behaviour of these sorbents in a desulfurization process.

XRD of the calcined sludge shows that in these ashes are present the same main crystalline compounds that in other calcined sewage sludge. CaO used as raw material is present in the sorbents as $\text{Ca}(\text{OH})_2$. In sorbents prepared in seawater, NaCl is always present as a component of the sorbent. The specific surface area of the sorbents increases as time and temperature of preparation does probably due to the formation of new products. Hydration of raw materials in seawater produce sorbents with slightly lower specific surface area comparing to sorbents prepared in distilled water at the same conditions.

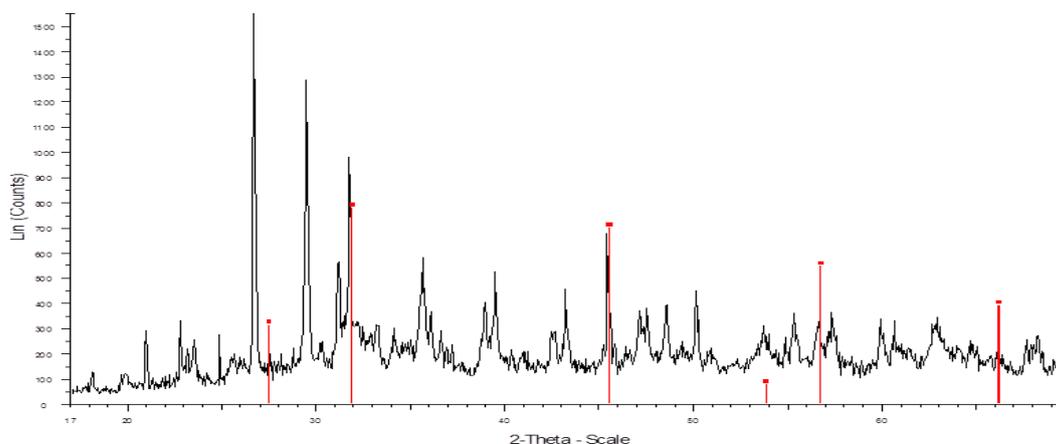


Figure 5. Diffraction figure of sorbent H with the diffraction pattern of NaCl overlapped.

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