Eur J Appl Microbiol Biotechnol (1982) 16:228–230

European Journal of Applied Microbiology and Biotechnology

© Springer-Verlag · 1982

Short Communication

Extraction of Aluminum from Fly-Ash by Commercial and Microbiologically-Produced Citric Acid

A. Singer, J. Navrot, and R. Shapira

Faculty of Agriculture, The Hebrew University of Jerusalem, Rehovot 76100, Israel

SUMMARY

Aluminum extraction from two aluminum-rich fly-ashes by commercial and microbiologically-produced citric acids was tested. Up to 12% Al_2O_3 of the total was extracted by a 21 hrs' shaking treatment at 60°C. Extraction efficiency is considerably affected by extracting acid concentration and extraction temperature. The extraction efficiency of microbiologically-produced citric acids was only slightly lower than that of commercial citric acid of equal molarity.

INTRODUCTION

All power-plants in Israel are at present fuelled by oil. Since Israel, however, lacks any natural oil resources, the gradual transition to power generation by other means has become mandatory. The first power plant to operate on coal is due to start production during 1982, and several others are being planned for the near future.

Since these power-plants will be situated in the most densely settled areas of the country, the accumulation of fly-ash, produced by the operation of the coal-burning power-plants, presents a major ecological problem. For the disposal of the fly-ash several uses have been proposed, such as for construction materials, amelioration of lands and fertilization of soils. All these proposals are not entirely satisfactory. This has led to a search for less conventional means for the economical use of fly-ash. One of these is processing for the separation and recovery of their mineral contents. Though today not less than in 1970 "it would take a drastic shift in economies and raw material availability to justify the expensive technology that would be required" (Outlook, 1970), it was felt that some preliminary studies would be useful for assessing the prospects.

Aluminum is enriched in fly-ash and its extraction appears therefore to be technically feasible. The choice of aluminum for the extraction trials has also been prompted by recent reports on the ability of organic acids to extract metals from various rocks and minerals. Huang and Keller (1970, 1971), and Huang and Kiang (1972) report on a considerable complexation of metals from various minerals and rocks, by organic acids, at room temperature. Singer and Navrot (1976) have demonstrated the extraction of metals from basalt by humic acids. Razzaghe and Robert (1979) have shown that from among 20 organic acids examined, citric acid was the most efficient for the extraction of aluminum from mica. Organic acids as extractants have the advantage that they can be microbiologically produced from agricultural waste products (Smith and Berry, 1975).

MATERIALS AND METHODS

The two fly-ashes used for the study were produced from bituminous coal deposits that are to supply the Israeli power-plant. One was taken from the Liddell power-plant in New South Wales, Australia. The second from the Le Havre, France, power-plant, with the coal originating in South Africa. The fly-ashes are very similar in Al_2O_3 contents (30.5 and 32.2%, respectively) while differing highly in their bases and silica contents (Ravina, 1979).

The microbiologically produced acid was obtained from a strain of Aspergillus niger ATCC 9142, known to produce citric acid, grown in submerged culture on a synthetic liquid medium containing 10% sucrose. After 30 days, the fungi were filtered through No. 42 Whatman filter paper and the filtrate was used for the extraction. The acidity of the acids was determined volumetrically using 0.1 mol.L^{-1}

Offprint requests to: A. Singer

0171-1741/82/0016/0228/$01.00

Table 1. Aluminum (expressed as Al_2O_3) extracted from South African and Australian fly-ashes, by 0.13 mol.L^{-1} citric acids, produced from Aspergillus niger cultures (MCA) compared to extraction by commercial citric acid of the same concentration (CCA). Ash: extractant ratio 1:100 w/w, shaking time 21 hrs. at 25°C and 60°C.

Citric acids	Al_2O_3 extracted from fly-ashes (%) South Africa absolute	South Africa of total	Australia absolute	Australia of total
At 25°C				
1 CCA	2.45	7.6	2.11	6.9
2 MCA	2.22	7.0	1.86	6.1
At 60°C				
1 CCA	3.89	12.2	2.94	9.6
2 MCA	3.50	10.9	2.62	8.6

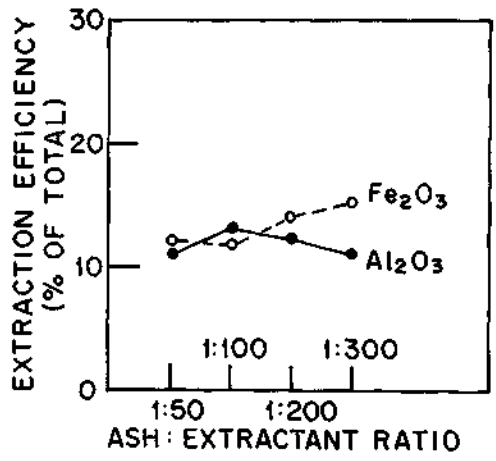

Fig. 1. Al_2O_3 and Fe_2O_3 extracted from South African fly-ash expressed as % of the total amounts (dry 105°C basis) after 21 hrs' shaking with 0.13 mol.L^{-1} citric acid at 60°C and at varying ash:extractant ratios.

NaOH and phenolphatein as indicator. The Aspergillus niger strain used in this study has recently been shown to grow on cotton waste, a waste product abundantly available in Israel (Kiel et al., 1981). In their work, Kiel et al. (1981) described two ways of fermentation, one in which sucrose was the sole carbon source, the second in which the fungus was first grown on cotton waste, followed by transfer to a sucrose media. In the present study, sucrose was used both for the fungus growth and the fermentation process. Implied is the suggestion that in this extraction process also cotton waste could replace sucrose in the growth stage of the fungus.

The concentration of the microbiologically produced citric acid was 0.13 mol.L^{-1}, therefore an equivalent molar concentration was prepared from commercial citric acid salt.

All extractions were performed in triplicate by shaking fly-ash with citric acid solutions on weight basis ratios (fly-ash: extractant) of 1 to 50, 100, 200 and 300, respectively. The shaking times were: 7, 14 and 21 hours at two temperatures 25°C and 60°C, using a water bath shaker. After filtration through a Whatman No. 42 filter paper, aluminum concentrations of the filtrate were determined by atomic absorption spectrophotometry using a Perkin-Elmer Model 2380 AAS and a nitrous oxide-acetylene gas mixture. The results are presented on dry fly-ash basis.

RESULTS AND DISCUSSION

Although the two fly-ashes are similar in total Al content, more aluminum was extracted from the South African fly-ash (Table 1).

More than 12% of the total Al were extracted from the South African fly-ash, at a fly-ash: extractant ratio of 1:100 w/w and at 60°C. At higher as well as at lower fly-ash:extractant ratios, the extraction efficiency decreased slightly (Fig.1).

In this test, the iron concentration in the extract was also measured. Contrary to aluminum, the iron extraction efficiencies increased significantly with the increase in the extractant to fly-ash ratio. This suggests equilibrium dissolution of a specific, relatively easily solubilized Al-bearing mineral phase in the fly-ash.

Temperature as well as acid concentration appear to have a great effect on extraction efficiency. The increase from 25°C to 60°C, increased Al extraction by about 59% from South African fly-ash and 39% from Australian fly-ash (Table 1). Decreasing citric acid concentration from 0.13 M to 0.013 M decreased extraction efficiency by 42% at 25°C and by 40% at 60°C.

Decreases in shaking time from 21 to 7 hours resulted in only slight decreases in extracted Al from both fly-ashes. The extraction efficiency of microbiologically produced

citric acid was only slightly lower than that of commercial acid of equal molarity. Results showed that with the South African fly-ash, the extraction efficiencies of the citric acids obtained by Aspergillus niger were 91% at 25°C and 89% at 60°C, compared to those of the commercial citric acid (Table 1). With the Australian fly-ash, the efficiencies of the microbiologically produced acids were 88% and 90% at 25°C and 60°C, respectively, compared to those of the commercial citric acid. This demonstrates the technical feasibility of using microbiologically produced citric acid of lower cost for the extraction of aluminum from suitable fly-ashes. Further studies involving, among others, the effect of shorter extraction times and narrower ash-extractant ratios, would be required for an assessment of the economic feasibility of the process.

CONCLUSIONS

Citric acid can extract significant quantities of alumina from aluminum-rich fly-ash. Alumina content alone does not appear to determine amounts of alumina extracted, since extraction efficiency differed between two fly-ashes, though they contained similar amounts of alumina. Extraction efficiency increases considerably with increases in extracting acid strength and extraction temperature. Extractant:ash ratio variations and extraction time variations do not appear to affect extraction efficiency significantly. This suggests equilibrium dissolution of a specific, relatively easily solubilized Al-bearing mineral phase in the fly-ash. The extraction efficiency of microbiologically produced organic acids is only slightly lower than that of commercial citric acid of equal acid concentration. This demonstrates the technical feasibility of using microbiologically produced acid extractants for the extraction of aluminum from suitable fly-ash.

ACKNOWLEDGMENT

The authors are indebted to Dr. D. Ravina of the Technion, Israel Institute of Technology, for providing the samples.

REFERENCES

Huang W H, Keller W D (1970) Dissolution of rock-forming silicate minerals in organic acids: Simulated first-state weathering of fresh mineral surfaces. Am Mineral 55: 2076-2094

Huang W H, Keller W D (1971) Dissolution of clay minerals in dilute organic acids at room temperature. Am Mineral 56: 1082-1095

Huang W H, Kiang W C (1972) Laboratory dissolution of plagioclase feldspars in water and organic acids at room temperature. Am Mineral 57: 1849-1859

Kiel H, Guvrin R, Henis Y (1981) Citric acid fermentation by Aspergillus niger on low sugar concentrations and cotton waste. Appl Environ Microbiol 42: 1-4

Outlook (1970) Fly-ash utilization climbing steadily. Environ Sci Technol 4: 187-189

Ravina D (1979) South African and Australian fly-ash as a mineral admixture to Israeli Portland Cement and Concrete. Building Research Sta Technion, Israel Institute of Technology, Report, 64 pp

Razzaghe M K, Robert M (1979) Geochemie des elements majeurs des micas en milieu organique; mecanismes de l'alteration des silicates. Ann Agron 30: 493-512

Singer A, Navrot J (1976) Extraction of metals from basalt by humic acids. Nature 262: 479-481

Smith J E, Berry D R (eds) (1975) The Filamentous Fungi. Vol. 1. Industrial Mycology, Edward Arnold Press, 740 pp.

Received November 18, 1982