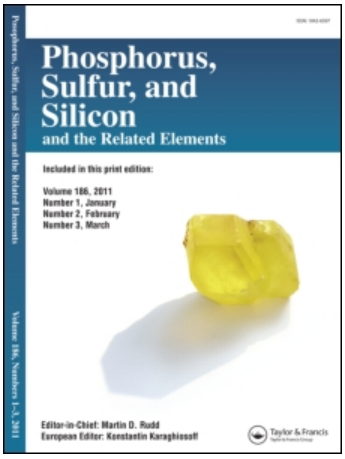

Phosphorus, Sulfur, and Silicon and the Related Elements

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BIOLOGICAL SEPARATION OF PHOSPHATE FROM ORE

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Abstract The importance of microbial action in mobilization of insoluble phosphate in soils is widely recognized though the process is not well understood. Based on literature reports and on an energy conservation potential, research on the potential of using biosolubilization for the industrial processing of rock phosphate ores appears to be worth while. This paper reports on efforts to develop such a process. Activities related to the isolation and selection of phosphate solubilizing microbial species as well as those efforts to develop a bench top bioprocess unit for the continuous solubilization of phosphate ore are discussed.

INTRODUCTION

Because of chemical precipitation and biological immobilization it would appear that without periodic replacement, the available supply of phosphate (PO_4) in soil would rapidly be depleted. This would be the case if it were not for the occurrence of PO_4 releasing mechanisms in soil. Microbial action appears to be one of the more important mechanisms for the rapid release of PO_4.

While the *in situ* agricultural use for these organisms has been studied for decades, their application for the industrial processing of rock phosphate ore (RP) has been ignored. Such a process could be used for partial replacement of current energy-intensive processes or in the recovery of PO_4 from low-grade and currently unusable RP ores. Another application could be the development of an inexpensive, low-technology method for PO_4 production in areas of the world which have RP reserves but lack sufficient capital and technology to develop the resource. The technology may also have a direct application for the removal of trace amounts of PO_4 from metal bearing ores. This paper discusses the first application, the development of a continuous process for the biosolubilization of PO_4 from the parent RP.

MATERIALS AND METHODS

Over 800 microbial colonies isolated from 54 different environmental samples were evaluated for evidence of PO_4 solubilization activity. Screening for active colonies was with the Katznelson and Bose agar plate bioassay[1]. Several isolates shown to possess the solubilization trait were selected for studies designed to evaluate a continuous

bioprocess methodology. The first study using these organisms was conducted using flasks containing liquid media (nutrient salts without PO_4; 1% glucose) and an insoluble source of PO_4 (initially tricalcium phosphate [TCP] followed by RP). Flasks containing media and selected inoculum were incubated on a shaker. After centrifugation to remove solids, the liquid from these flasks was analyzed to determine solution pH and the quantities of titratable acidity (H), soluble PO_4 (stannous chloride molybdate blue method), soluble calcium (Ca) (atomic adsorption) and organic acids (OA) (HPLC). All data were normalized based on ionic charge and reported in milliequivalences (meq).

From the above evaluations, a single bacterium (E37) was selected for additional studies in a continuous system. This system consisted of a continuous flow, stirred-tank bioreactor connected to secondary contact reactors (Fig. 1). The bioreactor was used for propagation of the bacteria. Initially it was one liter in volume and was operated

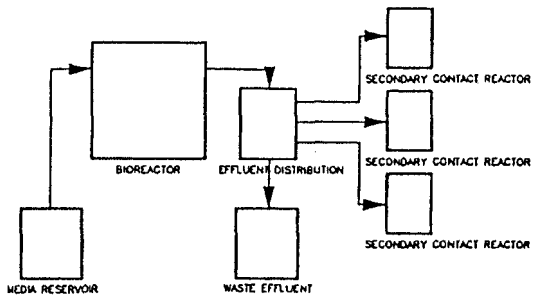

FIGURE 1 Schematic of process for continuous biosolubilization of RP.

under continuous flow conditions at a controlled pH of 3.4. Effluent (lixiviant) from this bioreactor was pumped into 125 mL contact reactors where it was mixed with RP. The effects on the solubilization process of various RP solids densities and lixiviant flow rates and quantities were evaluated using the secondary contact reactors.

RESULTS AND DISCUSSION

Numerous studies were conducted during the development of the continuous PO_4 solubilization process. For that reason, only data from those studies which advanced the work from elementary flask studies to the continuous bioreactor work will be discussed in this paper.

Phosphate solubilizing microorganisms are heterotrophic (i.e. energy and carbon are obtained by metabolizing organic compounds). In addition, it has been shown that the microbes responsible for solubilization utilize less than 1% of the PO_4 they solubilize[2]. Of the 860 microbes isolated in this study, 36% of the bacteria and 19% of the fungi were found to be active in solubilizing insoluble PO_4. Ten each of the most aggressive solubilizing bacteria and fungi were selected for liquid media shake flask studies. Of these, one bacterium (E37) and one fungus (I5G) were selected for in-depth studies.

The ability of E37 and I5G to solubilize TCP (19.3 meq PO_4 g^{-1}) and RP (13.3 meq PO_4 g^{-1}) under uninterrupted growth conditions was examined. Solubilization of TCP was investigated first. Over a four day time period, it was found that both organisms were capable of solubilizing 80% of the available PO_4 from TCP. In addition, there appeared to be a correlation between the amount of PO_4 solubilized and the production of soluble Ca, H, and OA. In the case of E37, all of the analytes were present in nearly equal quantities. With I5G there was a decrease of almost a factor of two between the amount of OA present and the other analytes. These data were sufficiently encouraging to justify repeating the study using RP as the insoluble PO_4 source. In this study 40% and 68% of the RP was solubilized by I5G and E37 respectively. As with the previous study there was good agreement between the amount of PO_4 and Ca solubilized and production of the other analytes.

Data from these two studies showed that a marked decrease in the pH of the growth media (at times less than pH 3) occurred during the first two or three days of a study. This decrease in pH was accompanied by an increase in soluble PO_4 and, for the bacteria, a concomitant decrease in viable organisms. To investigate this phenomenon, the effect of maintaining a nearly constant growth solution pH was investigated. This was accomplished by replacing growth media in each flask with fresh media every three days over a nine-day period. With the periodic media replacement, both the fungus and bacterium solubilized substantial quantities of RP (82 and 85% respectively). The most active period of solubilization was within the first six of the nine days.

Using the bioreactor design shown in Figure 1, several studies investigating the effect of various glucose concentrations, media flow rates, and RP solids were conducted. Only the bacteria E37 was used in these studies. Data from the initial studies showed that RP solubilization depended the glucose concentration of the growth media. Solubilization under continuous conditions stopped at a glucose concentration between 0.1 and 0.5% with the rate leveling off at concentrations greater than 1%. Apparently, this was related to the ability of the organism to produce OA at the various glucose concentrations, as well as its overall viability. At satisfactory concentrations of glucose (near 1%), RP at a solids density of 1% (1.33 meq of insoluble PO_4) was solubilized at a rate of 3.0 meq PO_4 L^{-1} lixiviant. Other studies showed that the quantity of PO_4 solubilized under continuous flow conditions at that rate was proportional to lixiviant flow but not RP solids density. When the media flow was increased from 200 mL d^{-1} to 400 mL d^{-1} in studies containing 1% solids density, the total quantity of PO_4 solubilized was noted to be increased dramatically (Fig. 2) at an elevated rate of 4.7 meq L^{-1}. At the same flow (but with a solids density of 10%) there was an increase in the rate of solubilization from 4.5 to 5.7 meq L^{-1} with a resultant 100% increase in the quantity of total soluble PO_4 (Fig. 3). Some 31% of the available 10 g of RP was solubilized.

Initial studies were conducted to determine how the process was affected by system scale-up. In these studies the volume of the bioreactor unit was increased to 10 L (10x) with a contact cell volume of 5 L (50x). Lixiviant flow from the bioreactor was maintained at 10 L

d^{-1}. A clarifier was placed in line with the out flow from the contact cell and served as a means to recover RP which had been hydraulically displaced. Using this newly designed system, studies were run at 5 and 10% RP solids densities.

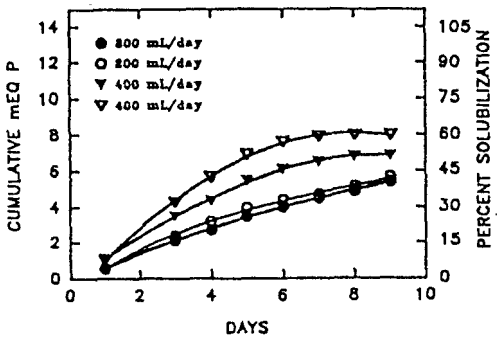

FIGURE 2 Effect of process solution flow on solubilization of 1 g RP.

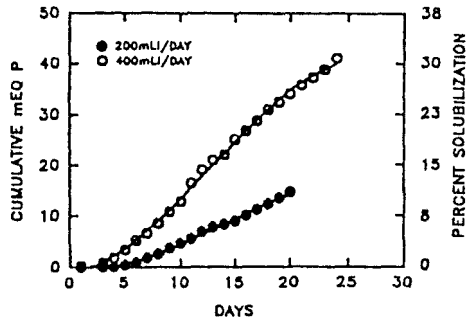

FIGURE 3 Effect of process solution flow on solubilization of 10 g RP.

Data from the studies showed the scale-up had minimal affect on the process of solubilization. At a 5% solids density, the rate of solubilization was 5.6 meq L^{-1} with 21% of the available PO_4 being solubilized over a 21 day time period. At 10% density, the solubilization rate increased to 7.3 meq L^{-1} which resulted in 15% of the available RP being solubilized within 21 days.

Results from these series of studies have demonstrated the feasibility of using a continuous bioprocess for the solubilization of RP. Additional studies will be needed to determine if the process can be scaled up to industrial capacity. However, some assumptions can be made based on the available data. Using initial calculations, it was estimated that the energy requirements for a bioleach process would be close to 5.02 MBtu ton^{-1} of RP processed. This represents a potential energy savings of 32 to 68% over the conventional processes[3]. The conceivable energy savings together with the opportunity to recover PO_4 from RP currently considered unfit for processing are considered sufficient reasons for continued development.

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