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Solubility Test of Partially Acidulated Sudanese Phosphate Rocks in Conventional Solvents

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ABSTRACT

Phosphate rocks are important in different industries as those of phosphoric acid and fertilizer. This study was carried out to test the solubility of Partially Acidulated Phosphate Rock (PAPR) from eastern part of Nuba Mountains area, namely J.Kurun. Colorimetric techniques were used for determination of the solubility in water, neutral ammonium citrate (NAC) and 2% citric acid (CA) at 200℃, 400℃ and 600℃. The water-soluble P_2O_5 of PAPRs of partial acidulation at same temperatures were ranged between 1.40%and 44%. NAC soluble P_2O_5, of3% H_2SO_4were ranged between (0.56%and 2.80%. The 2% citric acid soluble of PAPRs sample were ranged between 8.00%and 20.70%.

KEYWORDS:phosphate rocks, partially acidulated phosphate rocks, solubility determination, Phosphatic Fertilizers.

المستخلص

تكمن أُهمية الصخور الفوسفاتية بأنها تدخل في مختلف الصناعات مثلحامض الفوسفوريك والأسمدة. هدفت هذه الدراسة لاختبار الذوبانية للصخور الفوسفاتية المحمضة جزئياً من عينات الصخور المستجلبة من منطقة جبل كُرون في شرق جبال النوبة. استخدمت تقنية التحليل اللوني في تقدير ذوبانية الفسفور في كل من الماء ومحلول الامونيوم المتعادل و حامض الستريك 2% عند درجات حرارة C200° و C400° و C600°. تراوحت ذوبانية الفسفور في الماء بين1.4 % و 44% و محلول الامونيوم المتعادل بين 0.56% و2.80%. بينما تراوحت قيم ذوبانية حامض الستريك بين 8.00 و 20.70 %.

INTRODUCTION

Phosphorus (P) is critically needed to improve the fertility for crop production in large areas of developing countries. The high cost of conventional, water-soluble phosphorus fertilizers constrains their use by resource-poor farmers. Recently phosphate rock (PR) has been examined and used directly as a low-cost alternative fertilizer on tropical soils where indigenous deposits of PR are located. Partialacidulation of (PRs) to form (PAPRs) represents technology that can be used to produce highly effective P fertilizers from those indigenous deposits [(1,2)].Many studies were conducted in different area aspects[(3-5)]. Because of the availability of raw phosphate rocks in different parts of Sudan to form partially acidulated phosphate rock (PAPR), it is necessary to search for methods of treatment which allow to classification and use of the low-quality- (low reactivity) phosphate rock.The use of indigenous natural phosphate rocks had been recognized as available, low-cost alternative for the conventional water-soluble phosphorus fertilizers though they show large differences in their suitability for direct application and many factors influence their capacity to supply phosphorus to crops (6). Although the phosphate rocks with low reactivity may not be suited for direct application, their agronomic effectiveness can be greatly improved by such processes as partially acidulated(7).It has been shown that some partially acidulated phosphate rock (PAPR) can be agronomical and economically effective in crop production as compared with conventional, fully acidulated fertilizers,*e.g.*, superphosphate (SSP) and triple superphosphate (TSP) (8). Phosphatic fertilizers differ widely in their solubility in water and citrate solution(9). The solubility tests of phosphate rocks using chemical extraction methods are empirical. They offer a simple and rapid method for classifying and then selecting PRs according to their potential effectiveness. The most commonly used reagents arewater,neutral ammonium citrate (NAC), 2% citric acid (CA) and 2% formic acid (FA). The three-fold classification system of PR solubility (low, medium and high) in NAC, 2% CA and 2% FAare shown in (Table.1). The system was based on International Fertilizer Development Centre IFDC data for the relative effectiveness of extraction media and the results of a wide variety of laboratory experiments and field trials were reported(10).

Table1: Proposed classification of phosphate rock solubility for direct application.

Rock potential	Solubility (% P_2O_5)		
	Neutral ammonium citrate	Citric acid	Formic acid
High	> 5.4	> 9.4	> 13.0
Medium	3.2-4.5	6.7-8.4	7.0-10.8
Low	< 2.7	< 6.0	< 5.8

The term partially acidulated PRs (PAPR) describes two, but very similar in chemical composition products, i.e, P fertilizers produced under two distinct technological processes such as:

.Partially acidulated, .i.e., less than the stoichimetric amount of acid required for complete dissolution of PR with H_2SO_4 or H_3PO_4.

.Physical mixture of Single Super Phosphate (SSP) and PAPRs (reactive PRs).

Accordingly,processes of PR dissolution can be summarized as follows:(11).

$$Ca_{10}(PO_4)_6F_2 + y(6-x)\ H_2SO_4 + 3xy\ H_3PO_4 + H_2O \rightarrow y(6-x)\ CaSO_4 + (3+x)y\ (CaH_2PO_4)_2\ H_2O + (1-y)\ Ca_{10}(PO_4)_6\ F_2 + y\ CaF_2.$$

PAPRs are cheaper than fully acidulated Water Soluble Phosphate (WSP) fertilizers because less acid and energy is required per unit of phosphorus in the product.

In addition, PAPRs are often more concentrated than SSP. Thus, in some situations partial acidulation may be a preferred way of improving the effectiveness of imported PRs. Partial acidulation is one way to increase their water solubility. The major components in PAPR products are water-soluble mono-calcium phosphate and sparingly soluble-un-reacted PR [12]. The aim of this study is to discuss the solubility test of partially acidulated phosphate rocks, from Nuba Mountain namely Jebel Kurun area, western Sudan. There is agronomy need for more detailed information on the properties of phosphate rocks,of what partial acidulation of phosphate rock is important.In Sudan,Kurun deposits consist of metamorphic graphite schist, breccias, quartzite breccias and apatite and apatite phosphorite, local deposits of indigenous phosphate rocks are not acidulated to diverse their application increase their efficiencyand decrease their cost, as a fertilizers.

MATERIALS and METHODS

Twenty samples,collected from J. Kurun area,Nuba, Mountains, from eastern Sudan,were prepared at the Laboratory of the Geological Research Authority of Sudan (GRAS), Ministry of Minerals, for analysis. The samples were dried in an electric oven at 110℃ for 2 hours, then cooled and stored in desiccators for analysis. Five concentrations of sulphuric acidwere used to acidify the PRs: 3% , 5%, 10%, 30%and 50% H_2SO_4. The ratio of rock's weight to acid volume is 1:1 (w/v). Then the acidulated samples were dried under sunlight and were heated at various temperatures: 200℃, 400℃, 600℃, for 2.5hours.One gram of PAPRs samples were accurately weighed on a 9-cm filter paper, leached successively with small portions of distilled water, until the filtrate is 250 mL. The filter paper containing the residual was transferred to 250-mL volumetric flask containing 100 mL of ammonium citrate solution.The flask was closed with rubber stopper and shaked vigorously to disintegrate the filter paper. The volumetric flask was attached to a shaking apparatus in a constant temperaturewater bath at 65℃. Water adjust level in. The bathshould be adjusted above level of the solution in the flask. The flask was shaked every 5 minutes, for one hour , cooled, filtered and washed with hot water to 250 mL. The residual was transferred to volumetric flask and dissolved by heating with 35 mL of HNO_3 and 10 mL of concentratedHCl, cooled and diluted to 250 mL with distilled water. The WSP, NAC and citrate-Insoluble P were determined colorimetrically[13]. Yellow color complex was formed when a sample solution containing orthophosphate was added to a reagent containing ammonium metavanadate in concentrated $HClO_4$, was 5mL of original samples (PAPRs) were pipetted into a 100mL volumetric flask, 45mL of water were added, followed by a 20mL of molybdovanadate reagent within five minutes were added, diluted with water to the volume mark, well, take to stand for 10 minutes the absorbance was measured at 400nm against a blank prepared in the same manner.

RESULTS

A calibration curve of the absorbance of standard solutions of KH_2PO_4 was deduced and used to calculate the concentration of P_2O_5 in the samples solutions see (Figure 1).

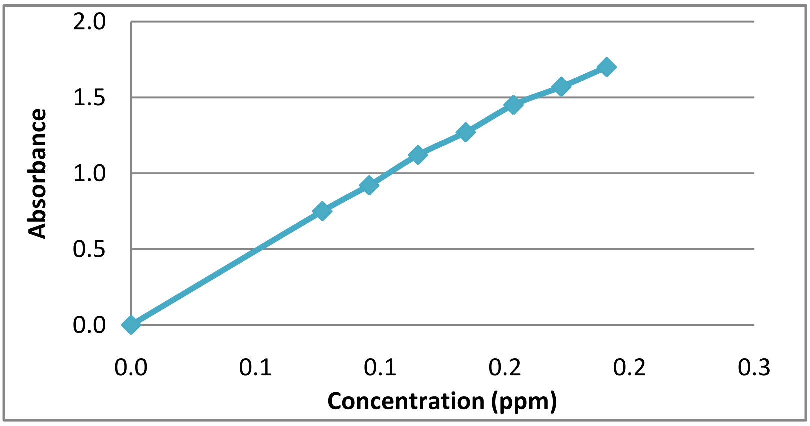

Figure 1: the absorbance of slandered solution of KH_2 PO_4

Peer's Law plot for phosphovenadomolybdate at 400 nm.The percentages of the solubility of PAPRs in WSP, NAC and CA solutions expressed as P_2O_5 percent is recorded in Table 2.

Table2: Chemical analysis and conventional Solubility of selected PAPRs of Sudanese PRs.

No.	**Percentage of H_2SO_4 acidulation%**	**Temp°C**	**Solubility expressed as total percentage of P_2O_5**					
			WSP	**NAC**	**W-In-SP**	**Available**	**Total**	**Citric acid 2%**
1	3	200	28	2.00	2.50	27.5	30.00	13.41
2	3	400	30	1.20	6.75	24.45	31.20	15.38
3	3	600	27	2.00	7.88	21.20	29.00	19.20
4	5	200	33	2.80	6.75	29.05	35.82	12.00
5	5	400	27	0.72	9.00	18.72	27.72	14.70
6	5	600	44	0.56	6.75	37.30	44.56	20.70
7	10	200	38	0.80	4.25	34.30	38.80	8.00
8	10	400	27	0.84	4.50	23.35	27.84	8.70
9	10	600	14	2.00	4.55	11.45	16.00	15.50
10	30	200	1.8	0.72	3.88	1.36	2.52	7.30
11	30	400	4	0.84	5.25	0.43	4.84	16.80
12	30	600	6	1.12	4.25	2.87	7.12	12.70
13	50	200	4	1.84	4.85	1.00	5.85	11.60
14	50	400	1.40	1.40	6.75	3.90	2.80	12.00
15	50	600	1.60	1.80	4.80	1.40	3.40	11.20
16	TSP		0.90	97	4.00	45.10	97.09	
Min			1.40	0.56	8.00	0.43	0.09	
Max			93.00	4.00	45.54	97.00	9.00	
Mean			23.74	1.54	32.02	20.96	5.18	
Median			27.00	1.30	39.10	19.96	4.83	
Std. Dev			23.45	0.92	13.69	24.02	2.15	
SEMean			5.86	0.23	3.54	6.00	0.54	

DISCUSSION

In the present work the Sudanese phosphate rocks were acidified by various concentrationsto enrich those contain proportion of 32.02% water-soluble-P, and 23.74% soluble in NAC and 25.29% citric soluble phosphorus. The first approach is solubility test of

PR using three chemical extractants. Solubility test using chemical extractantofferr a simple and rapid method for classifying and then selecting PRs according to their potential effectiveness [14]. The most common solutions are Neutral Ammonium Citrate (NAC) and Citric Acid (CA). The solubility data for these conventional reagents differ according to the strength of the extractants. This study consisted of a relative comparison of PRs from J. KurunNubaMountains area sources based on solubility experiments using solutions. These conventional solubility tests focus on the estimation of the temperatures and degree of partial acidulation of PRs. Table 2 shows that the NAC solubility of 3% H_2SO_4 at 200℃, 400℃ and 600℃ temperatures was ranged between 1.2% and 2.00%,. Those of 5% and 10% H_2SO_4, at same temperatures ranged between 0.56% and 2.80% and between 0.80%and 2.00% respectively. The Mean of NAC solubility of PAPRs was 23.74% Std. Dev 23.45%. However, water-soluble P_2O_5ranges of PAPRs for 3%, 5%, 10%, 30% and 50% H_2SO_4 at same temperatures were27% - 30%, 27% – 44%, 14% – 38%, 1.8% – 6% and 1.4% – 4.0%, respectively, indicating theinfluence of increasing the temperature. The presented high variability for (NAC+H_2O) soluble P_2O_5% (0.43% – 44.56%), water soluble- P_2O_5% (1.40-44.00%) and percentage of water-soluble soluble P_2O_5 in the NAC+H_2O fraction (0.43%- 97.00%), showed that the processes and materials, including the PR, used in the production of the P sources, interfered in the solubility of the PRs. Nevertheless based on current standards, Sudanese PRs meet the requirement to be commercialized as TSP (minimum 44% of water-soluble P_2O_5)[15].Analysis of the Sudanese PRs from J. Kurun area (Table 2) shows that they contained, appreciable quantities of PAPR,32.02% P_2O_5,compared with 35.86%$P_2O_5$of phosphate rocks ores. Being reactive, 25.29%P_2O_5 of their total phosphorus was soluble in 2% citric acid; they could, therefore, present excellent phosphorous sources for soil fertility by virtue of carbonate content express as 39.21% CaO. The acidulation of PR, from Jebel Kurun area,with 3%$H_2SO_4$to 30% H_2SO_4 increased WSP from 29% to 31% P_2O_5 and increased citrate solubility from 13.41% to 19.20%P_2O_5 representing total phosphorus.These increases of total a P were due to the increase of both concentrations and temperatures. There is no yet, general accepted classification system for rate grading of PRs quality according to their mineral composition. With the regard to chemical solubility,[16], the proposed a system for solubility ranking is stillhigh, medium, low and very low.

ONCLUSIONS

One of the reasons behind the rare use of the phosphate rocks as a direct application fertilizer is its solubility. To overcome this limitation, the partially acidulated phosphate rock was formed and has achieved a marked increase in the reactivity of the treated phosphate samples.The chemical reactivity of activated raw samples in 2% citric acid and neutral ammonium citrate, showed improved acidulation characteristics for all the pretreated samples.

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