

IFA Technical Conference

**Amman, Jordan
2-6 October 1994**

GRANULATION AND PARTIAL ACIDULATION OF EGYPTIAN PHOSPHATE FOR APPLICATION AS DIRECT FERTILIZER

Nagui A. Abdel-Khalek, N.A. El-Hussiny and M.E.H. Shalabi
Central Metallurgical Research and Development Institute (CMRDI), Egypt

RESUME

Cet exposé examine la possibilité de produire du phosphate partiellement acidulé (PAPR) à partir de fines de phosphate d'Abu Tartur au cours de leur granulation, pour application directe comme engrais. Ces fines contiennent beaucoup de dolomie et d'anckerite en plus de la pyrite et de la silice comme gangue associée. Des tests ont été effectués en utilisant H_2SO_4 98 % ou H_3PO_4 97 %. Les propriétés physiques des produits ont été déterminées en mesurant leur résistance à l'écrasement, leur résistance à l'abrasion et leur productivité tandis que leur réactivité chimique était mesurée avec l'acide citrique 2% et l'acide formique 4%.

Les résultats montrent que la production de PAPR avec H_2SO_4 85 %, H_2SO_4 98 % et H_3PO_4 97 % était techniquement possible jusqu'à 40 %, 50 % et 80 % de degré d'acidulation respectivement. A des degrés plus élevés, les granules obtenus deviennent collants et non maniables. La résistance à l'écrasement et à l'abrasion, pour des granules de - 4 + 1 mm, augmentait en même temps que le degré d'acidulation. Le P_2O_5 % total des produits était progressivement accru avec un apport accru de H_3PO_4 , tandis que dans le cas de l'emploi de H_2SO_4 , P_2O_5 % total était significativement réduit en raison de l'augmentation de la quantité de $CaSO_4$. La réactivité des produits dans l'acide citrique et l'acide formique augmentait en même temps que le degré d'acidulation. La réactivité était meilleure dans le cas de H_3PO_4 que pour H_2SO_4 . Par exemple, la réactivité pour H_2SO_4 85 % et H_3PO_4 97 % était augmentée de 3-4 et 5-7 fois respectivement, en comparaison des échantillons de phosphate d'origine. L'efficacité de ces PAPR est environ 90 % et 94 % de celles de SSP et TSP respectivement. L'application d'une technique de granulation à un seul étage/acidulation partielle peut aussi baisser les frais de fonctionnement en économisant 30-40 % des acides consommés pour SSP et TSP. De plus, les granules de PAPR obtenu satisfont les exigences locales de l'environnement et diminuent les pertes en cours de manutention et de transport.



KEYWORD: Phosphate; acidulation; granulation; reactivity; solubility; direct fertilizer.

INTRODUCTION

The bulk of today's worldwide phosphatic fertilizer is supplied as water-soluble salts of NH_4 or Ca. For example, concentrated superphosphate (CSP), monoammonium phosphate (MAP), diammonium phosphate (DAP), ammonium polyphosphate (APP), and nitric phosphate (NP). To prepare such high-analysis products, the fertilizer processes are based on phosphoric and nitric acid intermediates. However, this situation is now changing, due to the demands of environmentalists and conservationists as well as changing phosphorus fertilization requirements, and a partial transition to first-generation low-analysis phosphatic fertilizer materials as substitutes now appears unavoidable [1].

On the other hand, phosphate fertilizers with less water solubility are desirable in many tropical and subtropical countries. The phosphate deposits of such countries have little commercial significance due to either low grade, presence of excessive amounts of associated impurities or too unreactive. One means of economic utilization of such problematic ores is to increase the plant available phosphate by chemical conversion to a partially acidulated phosphate rock, PAPR, products [2]. The term PAPR refers to a phosphate rock that has been treated with an acid less than the stoichiometric amount required to fully convert the insoluble tricalcium phosphate, TCP, to the water soluble form [2]. The ability of this PAPR technology to cope with many types of phosphate rocks makes it possible to use indigenous raw materials widely spread in most developing countries. This technology is also used in some European countries, South Africa and Brazil [3]. The potential for adoption of this technology in West Africa and India are quite high [2]. In Israel commercial production of PAPR began in 1984 [4]. PAPR is also produced and marketed in substantial quantities in Germany and Finland [4].

The partially acidulated phosphate product can be powdery or semigranular, run-of-pile (ROP) material or granulated. A completely granular product can be made by granulating ROP material in a separate process, or it can be made directly by using a single-step acidulation/granulation process [2].

This paper presents the results of the single step granulation/partial acidulation of Abu Tartur phosphate fines, using H_2SO_4 or H_3PO_4 acid, for application as direct fertilizer. This type of ore contains a remarkable amount of associated gangues such as dolomite and pyrite. The partial acidulation tests are carried out in a laboratory disc pelletizer at the predetermined optimum conditions of the granulation process. The physical properties such as crushing strength and abrasion resistance of PAPER products as well as their chemical reactivities in citric acid and formic acid are investigated.

EXPERIMENTAL

Materials

A sample of Abu Tartur phosphate pre-concentrate (100% - 0.149 mm) was used in this study. The sample was prepared according to a pilot plant flowsheet adopted by CMRDI. XRD analysis showed that carbonate apatite is the principal phosphate mineral. Dolomite, montmorillonite, pyrite, gypsum and quartz are the minor constituents of the sample arranged in their increasing order of abundance. Table 1 shows the chemical analysis of the sample from which it is clear that the sample contains a relatively high percentage of Fe_2O_3 (~ 3.9%) due to the presence of pyrite. The sample has 3.6% MgO and about 11.2 wt% was lost by heating at 1000°C (L.O.I.) which reflected the presence of substitutional amounts of dolomite as XRD indicated. The reactivity of the sample in citric and formic acids are 20.36% and 24.39% respectively. The phosphate sample was ground to 100% - 200 mesh.

Sulphuric acid of different concentrations (85% and 98%) as well as phosphoric acid (97%), supplied by Abu Zaabal Fertilizers and Chemicals Co., were used in the partial acidulation tests.

Table 1: Complete chemical analysis of the phosphate sample

| Constituents | % |
|---------------------------|-------|
| Total P_2O_5 | 28.29 |
| CaO | 46.10 |
| MgO | 3.60 |
| SiO_2 | 3.10 |
| F | 3.00 |
| Cl | 0.01 |
| Al_2O_3 | 0.80 |
| Fe_2O_3 | 3.90 |
| Reactivity in citric acid | 20.36 |
| Reactivity in formic acid | 24.39 |

Methods

The granulation and partial acidulation tests are carried out in a single step using a 40 cm diameter and 10 cm depth, laboratory disc pelletizer. The tests were performed at the predetermined optimum conditions of granulation [5]. The required amounts of acid was sprayed onto the rolling bed of the material in the disc pelletizer. At the end of the test, the products were collected and screened to collect the (- 4 + 1 mm) fraction which was taken as a measure for the productivity of the process.

Crushing strength of the phosphate granules was measured using the standard methods of determining the physical properties of fertilizers established by IFDC, USA [6]. Measurement of abrasion resistance of samples was carried out using the rotary drum method [7]. This method was used to measure the abrasion resistance to dust formation as a result of granule-to-granule and granule-to-equipment contact. This test is very essential in determining material losses due to handling, storage and application [7].

A 6.35 cm length and 19.05 cm diameter stainless steel drum with a rubber-covered removable end plate supplied with a motor drive assembly and 50 stainless steel balls 7.9 mm diameter, was used for such purpose. The sample was first screened over 3.35 and 1.0 mm sieves. A 100 gm portion of - 4+1 mm fraction was weighed and charged to the drum together with 50 stainless balls. The drum was rotated for 5 min. at 30 rpm. The content was removed, hand screened over the 4.75 mm screen to remove the balls and finally mechanically screened on 1.0 mm sieve, the oversize of which was weighed. The degradation % was calculated as follows [7]:

$$\% \text{ degradation} = 100 - 100 \times \frac{\text{Wt. \% of - 4 + 1 mm fraction recovered}}{\text{Wt. \% of - 4 + 1 mm fraction charged}}$$

The solubility of samples was conducted by measuring the amount of P_2O_5 soluble in 2% citric acid or 4% formic acid. The chemical reactivity of a sample was calculated by multiplying the ratio of the soluble P_2O_5 in citric or formic acid to the total P_2O_5 % by [8,9].

RESULTS AND DISCUSSION

Granulation of Phosphate Fines

Partial acidulation tests were carried out in a laboratory disc pelletizer after optimizing the different parameters of the granulation process [5]. The optimum conditions for granulation of the phosphate sample (100% - 200 mesh) were as follows: moisture contents 15%; tilt angle of disc bottom 60°C; speed of the disc 17 rpm and residence time of 15 minutes. At such optimum conditions granules of crushing strength 630 g/granule with a productivity of about 62% were obtained [5]. These optimum conditions were applied during the partial acidulation tests.

Partially Acidulated Phosphates Using Sulphuric Acid

The simplified equation for the reaction of fluorapatite mineral with H_2SO_4 to form sulphuric acid base for partially acidulated phosphate rock (SAB-PAPR) or single superphosphate (SSP), normal superphosphate (NSP), is as follows:



The term y represents the degree of acidulation, i.e. $y = 1$ corresponds to acidulation for SSP production and $y < 1$ corresponds to acidulation for PAPR manufacture.

Effect of Partial Acidulation by H_2SO_4 on the Productivity and Mechanical Properties of Granules

Figures 1 and 2 show the influence of application 85% and 98% H_2SO_4 on the productivity and mechanical properties of the products respectively. The productivity of granules, while using 85% H_2SO_4 , was decreased at the beginning of acidulation (10%) from 62%, for the original sample to 43.3% and, then, it started to increase gradually at higher acidulation degrees up to 40% where it reached to its maximum value (56.7%). Increasing the acidulation degree above 40% deteriorated the productivity to nil, Figure 1. Similar trend was obtained while using 98% H_2SO_4 , Figure 2.

However, the productivity in the latter case reached to its optimum value (~ 81%) at 50% degree of acidulation. This optimum value (81% productivity) could not be obtained without acidulation or with application of 85% H_2SO_4 . The decrease in the productivity at 10% acidulation may be due to the vigorous reaction which takes place at such lower acidulation degree. The generated heat of reaction makes the product more dry and, in turn, difficult to granulate. The gradual increase in productivity, up to 40% in case of application 85% H_2SO_4 and 50% with 98% H_2SO_4 could be related to the formation of binding material such as $CaSO_4$. Above the optimum degree of acidulation the products become sticky and difficult to handle. This makes the productivity goes down to zero. The results in Figures 1 and 2 showed that it is possible to obtain granules at 50% acidulation in case of 98% H_2SO_4 while that is impossible to obtain with 85% H_2SO_4 . This may be due to the excess amount of water present in the latter case which gives a sticky and unmanageable product.

Figures 1 and 2 indicated also the results of the crushing strength of the produced granules. The crushing strength of the green granules increased slightly with increasing the acidulation degree while after 24 hours a remarkable increase in the crushing strength was noticed. The crushing strength was further improved after drying the obtained granules for one hour at 100°C. This may be due to increase of formation of the binding material ($CaSO_4$).

Figures 1 and 2 showed also a remarkable increase in the crushing strength with raising the acidulation degree. The crushing strength, which is measured after drying at 100°C, reached to its highest values (1733 and 1833 g/granule) at 40% and 60% acidulation degrees while using 85% and 98% H_2SO_4 respectively. It is clear that the acidulation process caused a remarkable improvement for the crushing strength of the produced granules in comparison with original phosphate sample (~ 630 g/granule).

The abrasion resistance of the partially acidulated granules was also tested the results of which are depicted in Figure 3. These results showed a gradual decrease in the amount of - 1 mm % after abrasion with increasing the degree of acidulation which means that the abrasion resistance of such samples increases after their partial acidulation, Figure 3.

Effect of Acidulation by H_2SO_4 on the Grade and Reactivity of the partially Acidulated Phosphate Granules

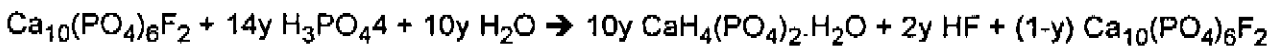
Figures 4 and 5 show the influence of degree of acidulation with H_2SO_4 of different concentrations on the solubility and reactivity of the produced granules. With 85% H_2SO_4 the total P_2O_5 content was gradually decreased from about 28.3% for the original sample to 20% with increasing the degree of acidulation to 60%, Figure 4. Similar trend was obtained while using 98% H_2SO_4 , Figure 5. Such decrease in the total P_2O_5 could be related to the increase in the amount of $CaSO_4$ in the granules.

Figures 4 and 5 indicated that the solubility and reactivity of the partially acidulated phosphates were significantly improved. The solubility in citric and formic acids of the partially acidulated granules were gradually increased with raising the acidulation degree. With application of 85% H_2SO_4 the solubility in citric and formic acids were increased from about 5.67% and 6.90% respectively, in the original sample, to their highest values (~ 16.2% and 17% respectively) at 60% degree of acidulation. This means that the reactivity at such conditions were increased from about 20.4% in citric acid and 24.45% in formic acid for the original sample to about 80.1% for the former and 83% for the latter, Figure 4. It is clear that application of 85% H_2SO_4 at 60% degree of acidulation can increase the reactivity of the granules by 3-4 times in comparison with the original phosphate sample.

Partial acidulation of phosphate with 98% H_2SO_4 (Figure 5) gave very similar results to that obtained with 85% H_2SO_4 (Figure 4). However, the reactivity of phosphate granules at 40-60% acidulation in case of 85% H_2SO_4 is higher than in the case of 98% H_2SO_4 . This may be due to the formation of some insoluble calcium phosphate compounds in the partially acidulated phosphate granules in the latter case. X-ray diffraction of phosphate sample acidulated with 98% H_2SO_4 at 60% degree of acidulation indicated that the main composition is a mixture of soluble Ca phosphate compounds and also $CaSO_4 \cdot 2H_2O$, Figure 6.

Phosphoric Acid Base for Partially Acidulated Phosphates

The reaction of H_3PO_4 with phosphate minerals (e.g. fluorapatite) to form phosphoric acid partially acidulated phosphate rock can be represented as follows:



The term y represents the degree of acidulation, i.e. $y = 1$ corresponds to acidulation for production of TSP whereas $y < 1$ corresponds to a partial acidulation.

Effect of Partial Acidulation by H_3PO_4 on the Productivity and Mechanical Properties of the Granules

Figure 7 depicts the relationship between the degree of acidulation by H_3PO_4 and the productivity of disc pelletizer and the mechanical properties of the produced granules. Partial acidulation with H_3PO_4 gave similar results to that obtained before with H_2SO_4 . However, the productivity of granulation with application of H_3PO_4 was much better where it reached to about 99.4% at 60% degree of acidulation and thereafter it decreased to 38% at higher acidulation degree.

Also, the crushing strength for the granules partially acidulated with H_3PO_4 behaves in a similar way to that produced with H_2SO_4 . However, the crushing strength in case of using H_3PO_4 was incomparable with that obtained with H_2SO_4 , i.e. replacing H_2SO_4 by H_3PO_4 caused a significant improvement in the crushing strength of the granules. It reached to its highest value (~ 4200 g/granule after drying) at 70% degree of acidulation while at 60% the crushing strength was about 3580 g/granule in comparison with about 1833 and zero g/granule in case of application 98% and 85% H_2SO_4 respectively. The results of testing the abrasion resistance for samples partially acidulated with H_3PO_4 was also better than in case of application of H_2SO_4 of different concentrations. With application H_3PO_4 the abrasion was lower at all degrees of acidulation in comparison with H_2SO_4 , Figure 3. It is clear that the mechanical properties of the produced granules was significantly improved when H_3PO_4 was applied.

Effect of H_3PO_4 Acidulation on the Chemical Reactivity of Phosphate Rock

Figure 8 shows the total P_2O_5 and solubility and reactivity of the products partially acidulated with H_3PO_4 . The curve of the total P_2O_5 gave a trend different from that obtained while using H_2SO_4 , i.e. the total P_2O_5 content was gradually increased from about 29.6% to 48.7% with increasing the degree of acidulation from 10 to 70% respectively while a reverse trend was obtained with H_2SO_4 . This is due to avoiding the precipitation of gypsum in case of phosphoric acid .

Figure 8 shows also the results of the solubility and reactivity of the products in citric and formic acids. The solubility in citric acid was successively increased from 13.1% to 37.6% with increasing the degree of acidulation from 10 to 70%. This means that the reactivity was increased from about 45% to 76.6%. Similar results were obtained with formic acid where the solubility and reactivity increased, from about 16.3 to 39% and from 56% to 80% respectively, with raising the acidulation degree from 10 to 70%. These results indicated that the solubility of such partially acidulated phosphates in acids could be increased by more than 5-7 times in comparison with the original phosphate rock. It is clear that the solubility and reactivity of the partially acidulated phosphates with H_3PO_4 are better than in case of using H_2SO_4 . This is due to the formation of gypsum in the latter case while with H_3PO_4 such precipitation of gypsum does not take place.

This was also confirmed in the XRD of the granules partially acidulated with H_3PO_4 at 60% degree of acidulation which indicated that the main phases are present as soluble compounds like $CaHPO_4$ and $Ca(H_2PO_4)_2$. Figure 6.

Technical and Economic Evaluation of the PAPER Products in Comparison with SSP and TSP

Figure 9 represents a flowsheet for the granulation/partial acidulation one step process while Table 2 shows the solubility of the PAPER products, obtained at the optimum conditions, and their consumption of H_2SO_4 or H_3PO_4 in comparison with those of single super phosphate (SSP) and triple super phosphate (TSP).

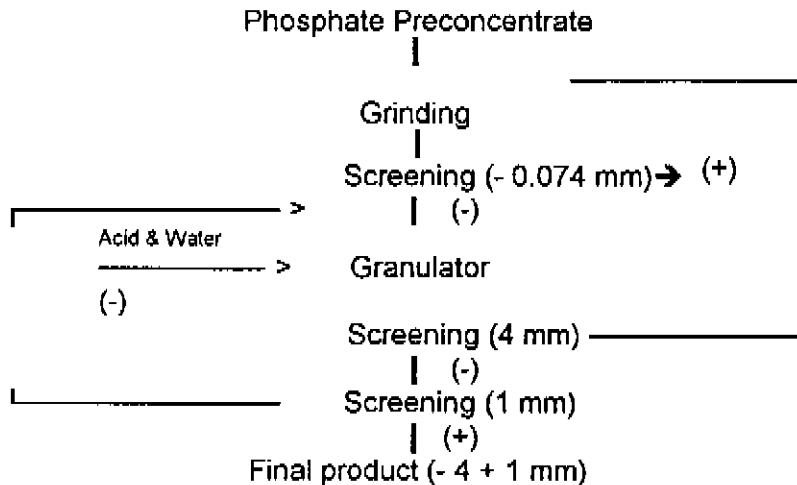


Figure 9 - Flowsheet of the granulation/partial acidulation process

Application of 85% H_2SO_4 at 50% degree of acidulation produced a product with a solubility in citric acid of 16.2% in comparison with 18% for SSP. This means that the efficiency of this PAPER product is about 90% of SSP. Also, application of H_3PO_4 at 70% degree of acidulation produced a partially acidulated product with a solubility of 37.5% in comparison with 40% for TSP which means that the efficiency of this product is about 94% of TSP.

Table 2: Solubility and acids consumption of PAPER, SSP and TSP

| Product | % Sol. in citric acid | Efficiency % | Consumption kg/t | % Save in acid |
|------------------------------------|-----------------------|--------------|------------------|----------------|
| (H_2SO_4 base) | | | | |
| SSP | 18.0 | | 791.6 | |
| PAPER | 16.2 | 90% of SSP | 475 | 40 |
| (H_3PO_4 base) | | | | |
| TSP | 40.0 | | 1360 | |
| PAPER | 37.6 | 94% of TSP | 952 | 30 |

It is clear that application of the PAPER technique can produce products with an efficiency (90-94%) near from SSP and TSP.

Moreover, application of the PAPR can reduce, from the economical point of view, the acids consumption in comparison with SSP and TSP. Production of a PAPR product with H_2SO_4 or H_3PO_4 base needs about 475 kg/t of the former acid or 952 kg/t of the latter acid in comparison with 792 kg/t of H_2SO_4 and 1360 kg/t of H_3PO_4 taken for producing SSP and TSP respectively. This means that application of the PAPR technique can cut down the operating cost by saving 40% of the H_2SO_4 and 30% of the H_3PO_4 required for SSP and TSP production.

Also, production of the partially acidulated products as granules satisfies the local environmental requirement and decreases the losses due to handling and transportation.

CONCLUSIONS

1. Production of partially acidulated phosphate granules from Abu Tartur ore using 98% and 85% H_2SO_4 was technically possible till 50% and 40% degree of acidulation respectively. At such degrees of acidulation the productivity reached to its highest values whereas higher degree of acidulation than these values got sticky and unmanageable granules. The crushing strength and abrasion resistance increased with increasing the acidulation degree due to the increase in the binding material (CaSO_4) formation.
2. The total P_2O_5 of the granules obtained with H_2SO_4 was gradually decreased with raising the acidulation degree due to the increase in the amount of CaSO_4 . The reactivity of PAPR in citric and formic acids was significantly improved with raising the acidulation degree. At 60% degree of acidulation with 85% H_2SO_4 the reactivity was increased 3-4 times in comparison with the original ore.
3. Production of partially acidulated granules using 97% H_3PO_4 was technically possible till 60% degree of acidulation at which the maximum productivity (~ 99.4%) was obtained. The crushing strength and abrasion resistance of the obtained granules were better than in case of using H_2SO_4 .
4. Application of H_3PO_4 in the partial acidulation of phosphates caused a remarkable increase in each of the total P_2O_5 and the reactivity of the end product where the reactivity was increased by more than 5-7 times in comparison with the original samples. Such reactivity (~ 81%) was also higher than that obtained while using H_2SO_4 . This is due to avoiding the precipitation of gypsum which takes place in case of H_2SO_4 application.
5. Application of the single step granulation/partial acidulation technique can produce PAPR products with efficiencies of 90% of SSP and 94% of TSP and, also, cut down the operating cost of the process by saving 30-40% of the acids consumed in SSP and TSP. Moreover, the produced PAPR granules satisfy the local environmental requirement and decreases the losses due to handling and transportation.

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Fig.1.Effect of acidulation degree on productivity and crushing strength (C.S.) of granules using 85% H₂SO₄

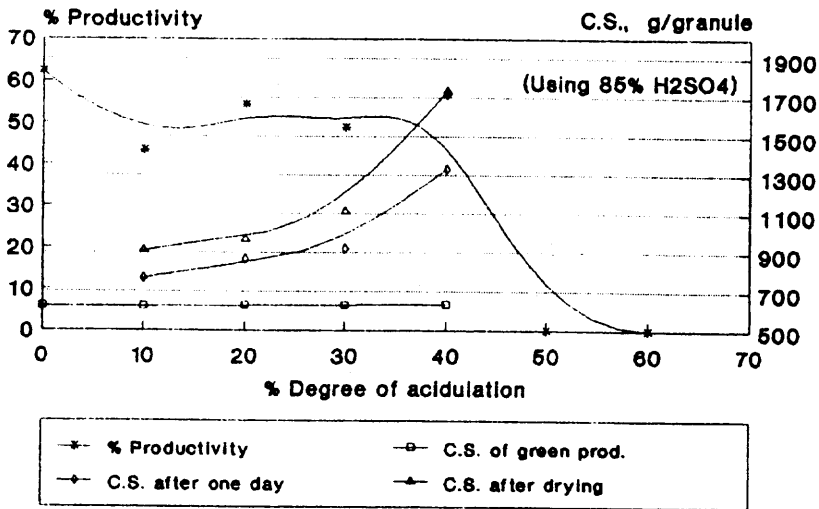


Fig.2.Effect of acidulation degree on productivity and crushing strength (C.S.) of granules using 98% H₂SO₄

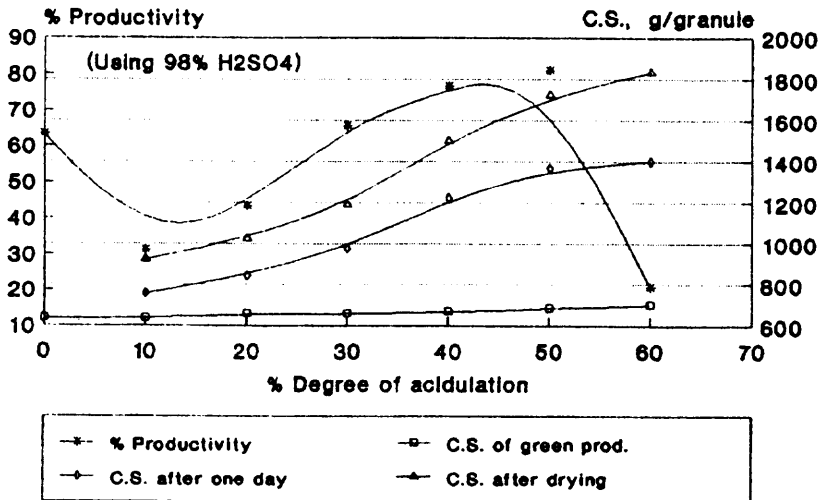


Fig. 3. Effect of degree of acidulation of different acids on the abrasion of the granules

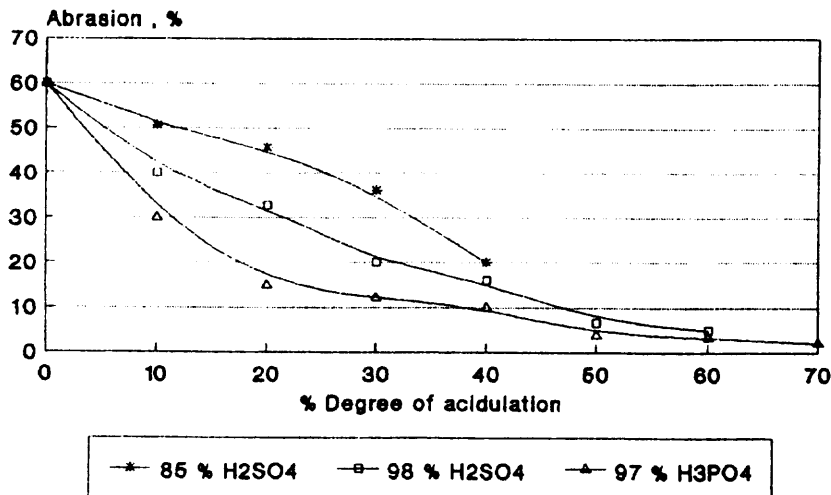


Fig. 4. Effect of acidulation degree on the solubility and reactivity of the produced granules using 85 % H₂SO₄

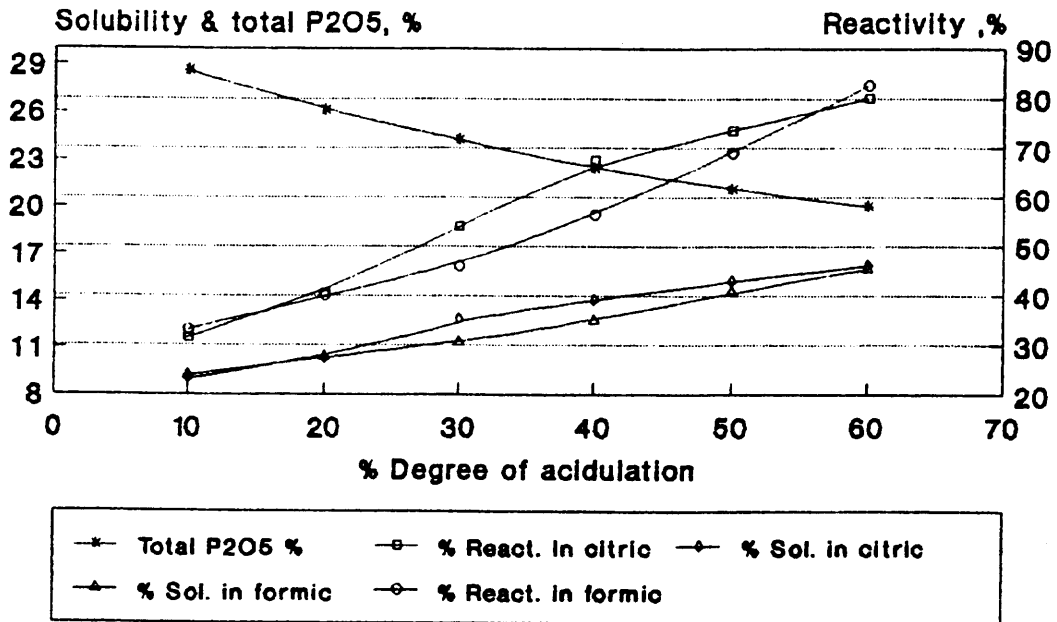
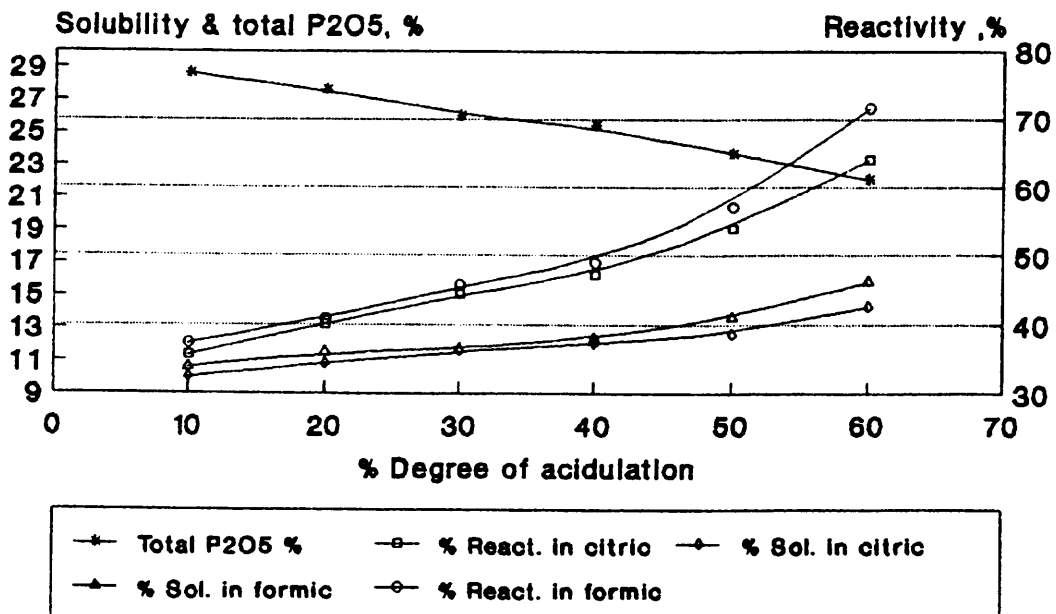


Fig. 5. Effect of acidulation degree on the solubility and reactivity of the produced granules using 98 % H₂SO₄



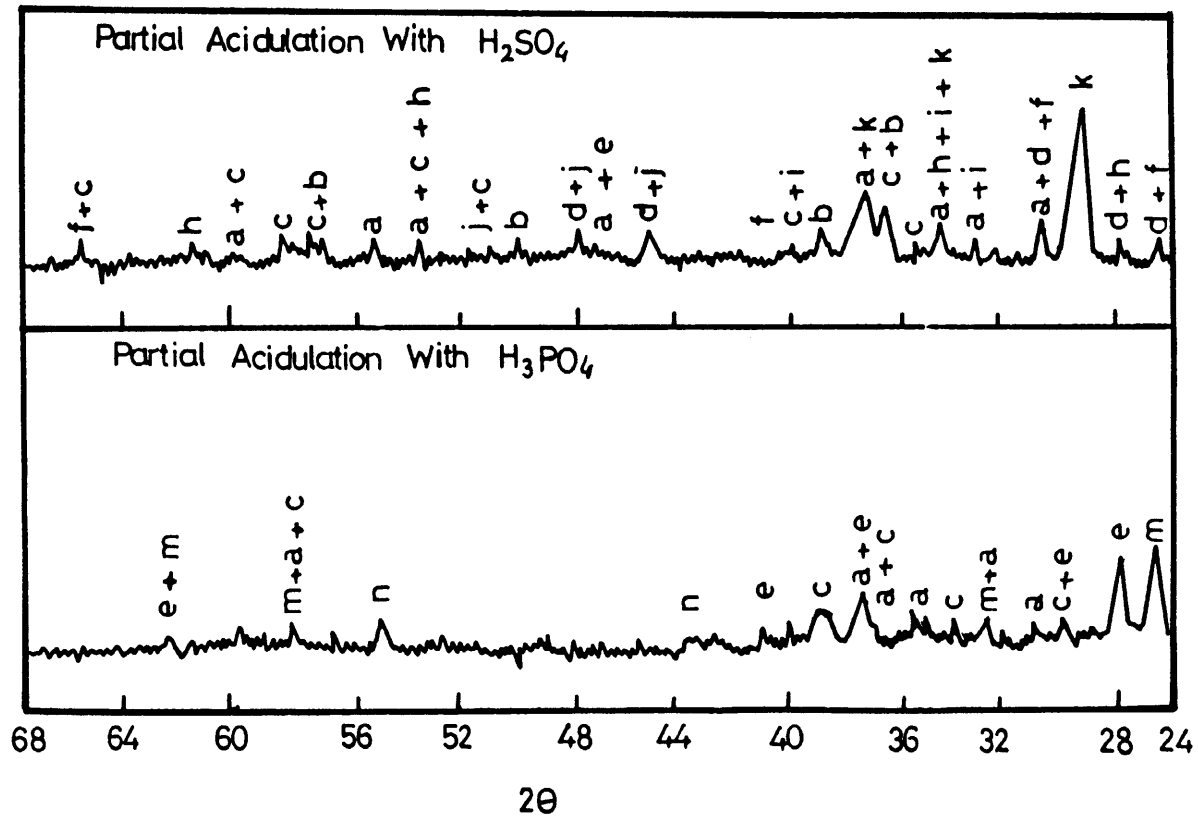


Fig. 6. XRD of the partially acidulated products.

| | | |
|-------------------------------|------------------------------|--------------------------|
| a- $CaHPO_4$ | b- $CaSO_4 \cdot 2H_2O$ | c- $CaHPO_4 \cdot 2H_2O$ |
| d- $Ca(H_2PO_4)_2 \cdot H_2O$ | e- $Ca(H_2PO_4)_2$ | f- $MgSO_4 \cdot H_2O$ |
| h- $Ca(H_2PO_2)_2$ | i- $Ca(PO_3)_2$ | j- $CaSO_4$ |
| k- $CaSO_4 \cdot H_2O$ | m- $Ca_3(PO_4)_2 \cdot H_2O$ | n- quartz |

Fig.7.Effect of acidulation degree on productivity and crushing strength (C.S.) of granules using 97% H3PO4

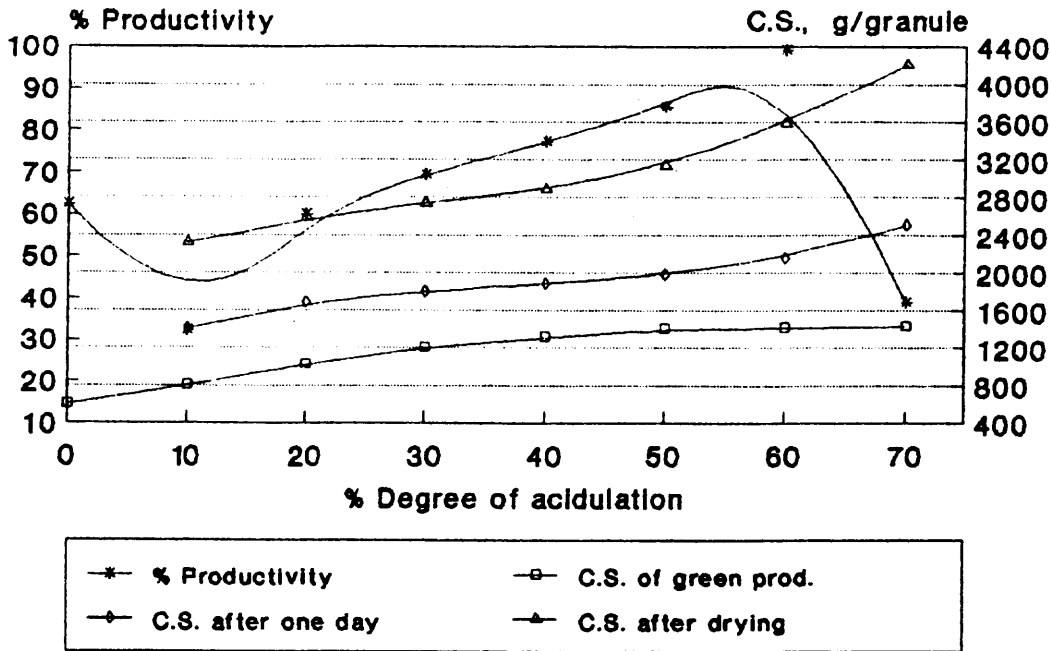


Fig. 8. Effect of acidulation degree on the solubility and reactivity of the produced granules using 97 % H3PO4

