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CONTRIBUTIONS TO THE BASES OF CONTROL OF SUPERPHOSPHATE MANUFACTURE.

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The simple superphosphate industry, which is about a century old and which is meeting at present several competitors, did not receive the adequate attention of scientists. This led to the result that the advances attained in the mechanical processes of the industry were not accompanied by equivalent advances in the chemistry of superphosphate. Thus, the industry has for a long time run without rules illustrating the optimum conditions, or establishing the relation between rock phosphate and the manufactured superphosphate.

The work of Shoeld, Wight and Sauchelli (4) in 1949, involving the study of "Rock-acid ratio in superphosphate manufacture", has been an important contribution in the field of the control of the process, in view of the "available" P_2O_5. No mention was made of the water soluble P_2O_5. An important result at which they arrived is that it is not important to get a superphosphate with maximum conversion and minimum insoluble P_2O_5; thus it may be more economic to get a superphosphate containing more insoluble P_2O_5 than the minimum. To verify this fact, they developed the cost curves for different grades of Florida pebble rock phosphates, which illustrated the relation between the percentage conversion and the raw material cost per unit available P_2O_5. It has been found that there is an optimum ratio of rock and acid at which the cost per unit available P_2O_5 comes to a minimum, which rises with further increase in percentage conversion. They also mentioned that the percentage of carbonate in the rock is an important factor, as any rise in this content means the consumption of more acid, followed by an increase in the values of raw material cost.

The present author (2) studied some factors affecting the system "Moisture-free phosphoric acid - water soluble P_2O_5 - total P_2O_5"; mention should be made here that the term (equilibrium) was improperly applied in place of the term (system). The work, which was based on the preparation of laboratory superphosphate samples, represented the first laboratory study in this field. The water soluble P_2O_5 was given the major importance as it is the measure of availability of superphosphate in this country. The "acidulation diagram" was a useful means of representation of the effect of quantity of acid per fixed quantity of rock and of the effect of ageing, on the above mentioned system. The work was carried out on an Egyptian Sibaiya phosphate rock, and the analyses of this type of rock, together with that of another type mined in the same district, were given. As these two types A and B were used in the present investigation, the chemical and screen analysis of the two samples are found in the following table.

INGREDIENTS	% in sample A	% in sample B
Moisture	1.31	0.96
Tricalcium phosphate	64.97	65.98
Calcium carbonate	11.26	8.53
Calcium fluoride	2.77	3.12
Fe & Al oxides	2.18	3.74
Calcium sulphate	1.67	0.33
Sodium chloride	0.45	0.07
Insoluble portion	6.56	10.76

Particle size, microns	% of sample A	% of sample B
More than 180	3.7	2.1
180 - 142	5.2	4.2
142 - 118	5.1	4.2
118 - 75	16.7	17.5
less than 75	69.3	71.9

The acidulation diagram of sample A at a room temperature of 28-29°C is found in figure 1. As mentioned before in (2), the water soluble P_2O_5 curves before and after ageing intersect at a point corresponding to a quantity of acid of about 170 grams per 200 grams ground rock. This point represents no change in the water soluble P_2O_5 on dry basis with ageing. The concentration of acid used throughout was 68.94% H_2SO_4 by weight. The present investigation involves the study of the following factors, which are related to the control of the process.

1. <u>The Production Factor</u>.

It is a common practice in several works to calculate the yield of superphosphate produced by multiplying the weight of ground phosphate by a certain factor, the production factor, which thus equals the weight of superphosphate over that of phosphate used. This factor depends on the following factors:

1. The quantity of acid applied to the rock.
2. The percentage of moisture in superphosphate.
3. The type of rock used.

As the moisture content is highly affected by the room temperature, it follows that the latter will affect the production factor. Figure 2 represents the effect of room temperature on the moisture contents of superphosphate samples, prepared from fixed quantities of rock sample A (200 grams each) and rising quantities of acid. Figure 3 illustrates the effect of quantity of acid on the production factor for sample A and the effect of room temperature on the curve, while figure 4 illustrates the same for sample B.

It appears that the production factor for a certain rock is variable through a considerable range, and that it is necessary to correct it according to the analysis of superphosphate. The moisture and free acidity will be the control factors; and it is preferable to make a set of curves for a certain sample of rock, plot between the production factor and the moisture content of superphosphate. Each curve will correspond to a definite value of free phosphoric acid calculated on dry basis. Thus, it will be possible for the manufacturer to make a careful control over the production factor and to calculate accurately the weight of superphosphate produced. In case it is required to make any changes in the running conditions of the plant, the factor can be changed accordingly by a knowledge of the analysis. Comparison of figures 3 & 4 shows how the type of rock should be taken into consideration. As example, we find that the superphosphate samples prepared from the same quantities of rocks A & B and the same quantities of sulphuric acid (160 grams each) and at the same room temperature (28-29°C) have the production factors 1.544 and 1.585 respectively. In addition the production factors for the same sample obtained from phosphate A is 1.544 at the summer room temperature and 1.680 at the winter room temperature. Details concerning the preparation of laboratory superphosphate samples have been mentioned before (2).

2. The Raw Material Cost per Unit Water Soluble P_2O_5.

If a certain weight of rock phosphate is treated with a certain weight of sulphuric acid, so as to produce a weight w of superphosphate containing x% water soluble P_2O_5, the number of units water soluble P_2O_5 will = w x. If the total cost of the amounts of rock and acid used is C, then the raw material cost per unit water soluble $P_2O_5 = \frac{C}{w\,x}$.

The curves in figure 5 represent the effect of quantity of acid on the material cost per unit water soluble P_2O_5. They have been plotted from data obtained from the acidulation of samples A & B at a room temperature of 28-29°C. The curves are of the same shape as those obtained by Shoeld, Wight and Sauchelli (4) for the cost per unit available P_2O_5. It can be seen that the quantities of acid 170 grams and 165 gms. per 200 grams of samples A & B respectively represent the optimum quantities at which the cost values per unit water soluble P_2O_5 come to a minimum. It can also be seen that the cost curve of sample B assumes a higher position than that of sample A. It may be worth noticing that the sample B contains less calcium carbonate than sample A. Shoeld, Wight and Sauchelli took the carbonate content as the only factor responsible for the rise in cost, while it has been found above that the cost values of the sample with lower carbonate content are higher than those of the other. This may probably be attributed to the higher iron and aluminium oxides content of sample B, a factor which is responsible for lower recovery values and accordingly a lower number of units of water soluble P_2O_5. The recovery curves for the two samples at the same room temperature, before and after ageing, are found in figures 6 & 7. It can be seen that the maximum recovery values are 93.7% and 87.9% for samples A & B respectively after ageing, and that the curves of sample A, before and after ageing, intersect at a point corresponding to 170 grams acid. However, the curve after ageing for sample B assumes a lower position than the original curve, indicating a drop in the percentage recovery values of low acidity samples and a slight drop in case of high acidity samples.

The final result is that the optimum quantity of acid required by certain rock phosphate, ground to a certain degree of fineness, is not necessarily that which gives maximum conversion. Thus, the optimum quantity of acid for sample A, at which the cost per unit water soluble P_2O_5 is minimum, gives a recovery value of 89% after the ageing period, while values as high as 93.7% are attained uneconomically by the application of higher amounts of acid.

Referring to figures 1 and 6, it will be found that the quantity of acid of 170 grams per 200 grams of rock A corresponds

1. The break point in each of the moisture and free acidity curves.
2. The intersection point between the water soluble P_2O_5 curves before and after ageing, at which no change takes place in the water soluble P_2O_5 value, calculated on dry basis, with ageing.
3. The intersection point between the percentage recovery curves before and after ageing, at which no change takes place in the percentage recovery value with ageing.

As regards sample B, no intersection has been found to take place between the water soluble P_2O_5 curves or the recovery curves, due to the reversion occurring during the ageing period. The optimum quantity of acid was found to correspond to the break points in the moisture and free acidity curves.

THE SYSTEM "FREE PHOSPHORIC ACID-WATER SOLUBLE P_2O_5-

CITRATE SOLUBLE P_2O_5- TOTAL P_2O_5".

In the water insoluble P_2O_5 region, existing between the water soluble P_2O_5 and the total P_2O_5 curves in the acidulation diagram (figure 1) are two components: the citrate soluble and the insoluble phosphates. To complete the diagram, it was decided to study the system "Free phosphoric acid - Water Soluble P_2O_5 - Citrate Soluble P_2O_5 - Total P_2O_5" on dry basis under fixed conditions. It was assumed that the system would attain equilibrium after the 33 days ageing period. At equilibrium the acidulation diagram may possibly represent a part of a diagram which illustrates the action of sulphuric acid upon the insoluble phosphates contained in the rock, and calculated as P_2O_5 on dry basis; this diagram being similar to phase diagrams.

For this purpose, acidulation of sample A was carried out at a room temperature of 29°C, and the resulting superphosphate samples analysed after 33 days. In the diagram in figure 8, the component A is the sulphuric acid of specific gravity 1.6020 at 20°C, while the component B is the rock phosphate containing 30.15% P_2O_5 on dry basis. In this diagram, the acidulation diagram lies in the region between 42.86 and 50% A. The point a represents 100% B and 0.0% A (i.e. 30.15% P_2O_5), while the point g represents 100% A (i.e. 0.0% P_2O_5). Starting from the point f, the addition of sulphuric acid will result in a decrease in the total P_2O_5 content along the line f g. From the point b, the formation of citrate soluble phosphates (mainly dicalcium phosphate) begins and proceeds along the line b h, which is the boundary between the insoluble phosphates existing in region P and the citrate soluble phosphates existing in region Q. From the point c the formation of water soluble phosphates starts along the line c e, which is the boundary between the water soluble phosphates existing in region R and the citrate soluble phosphates in Q. In the same way the line d e represents the boundary between the region of free phosphoric acid and that of water soluble phosphates.

If the composition of the mixture is represented by a point lying between a and b, the resulting system at equilibrium will consist of one component, namely insoluble P_2O_5. Between b and c, any composition will give rise to the two component system: citrate soluble and insoluble P_2O_5, while the compositions between c and d will give rise to the three component system; water soluble - citrate soluble - insoluble P_2O_5. The four component system: free phosphoric acid - water soluble P_2O_5 - citrate soluble P_2O_5 - insoluble P_2O_5, exists in equilibrium when the composition of the mixture is beyond the point d, till below e.

Methods of analysis of Superphosphate.

Free phosphoric acid: The titration of free phosphoric acid to the methyl orange end point, although adopted throughout this work, does not give exactly the free phosphoric acid content in superphosphate. This fact has been proved experimentally by the author (3). The method, however, can be regarded as suitable for comparison purposes and for the routine control of the plant.

Water soluble and total P_2O_5: These are of major importance in the process control. Much attention has been directed to the development of new methods to replace the long double precipitation method. The comprehensive study of Kassner & co-workers (1) led to the development of a rapid method for the estimation of P_2O_5 in rock phosphate. This method has been applied by the present author for the determination of water soluble and total P_2O_5 with satisfactory reproducibility with the double precipitation method.

CONCLUSIONS.

It has been possible to correlate the rock phosphate and the superphosphate with economic factors which can be controlled by chemical analysis. To run on such economic basis, it may be necessary to modify the conditions according to the type of plant, the type of rock and to the other prevailing conditions. The method adopted by the author for the laboratory acidulation of a certain rock enables the manufacturer to obtain rapid and accurate data, so that within a few weeks he can make up the plan according to which the plant will be run most economically and most satisfactorily.

LITERATURE.

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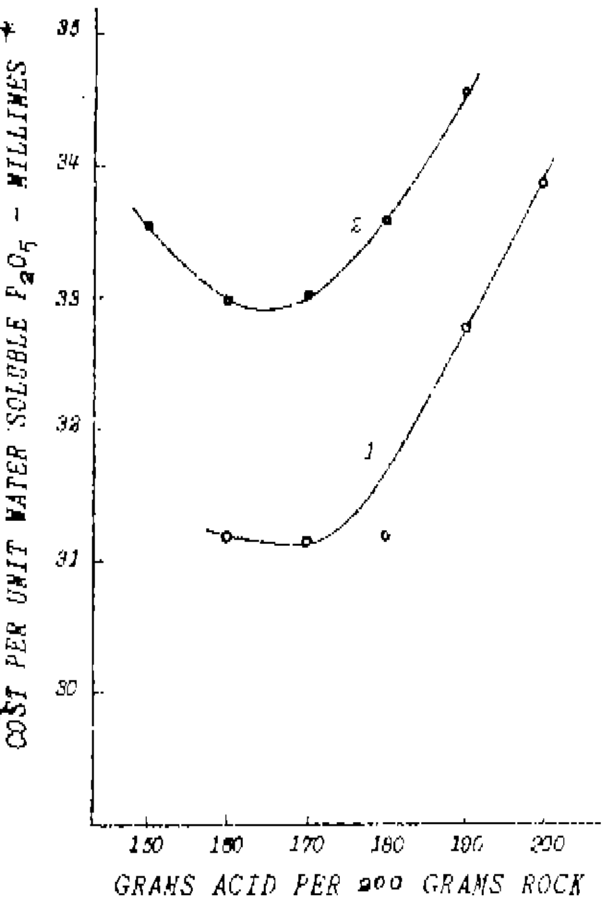


FIG. 5

1. Curve for sample A.
2. Curve for sample B.

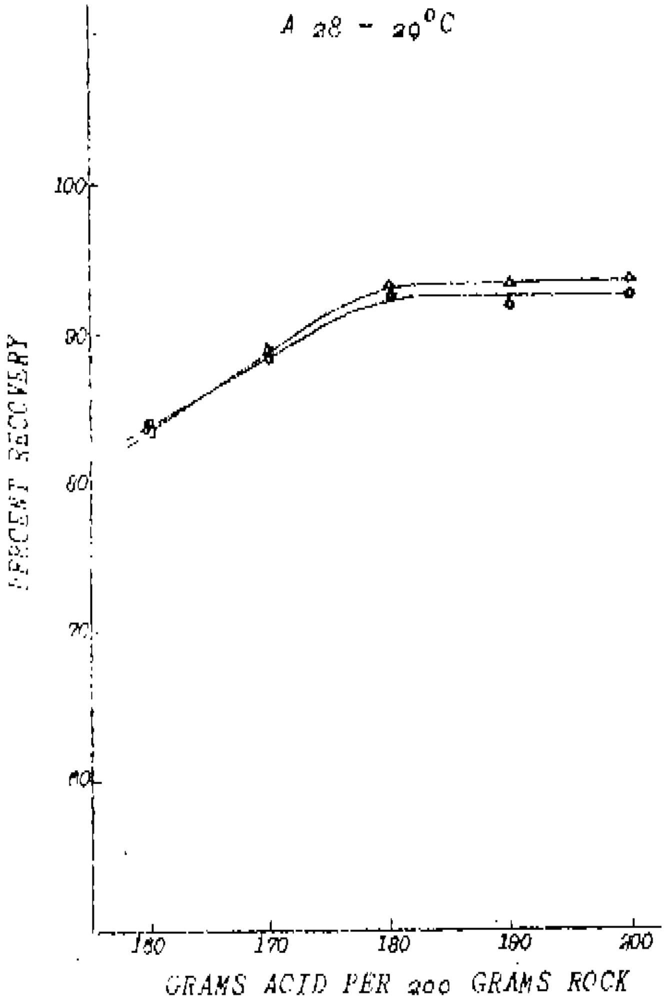


FIG. 6

o Three days after preparation
△ After 30 days ageing.

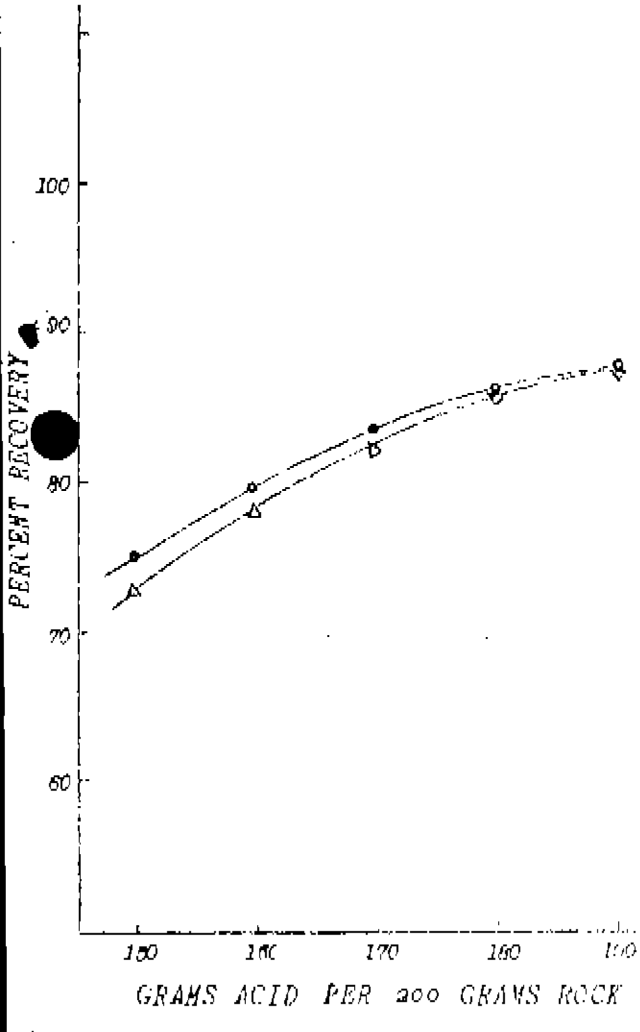
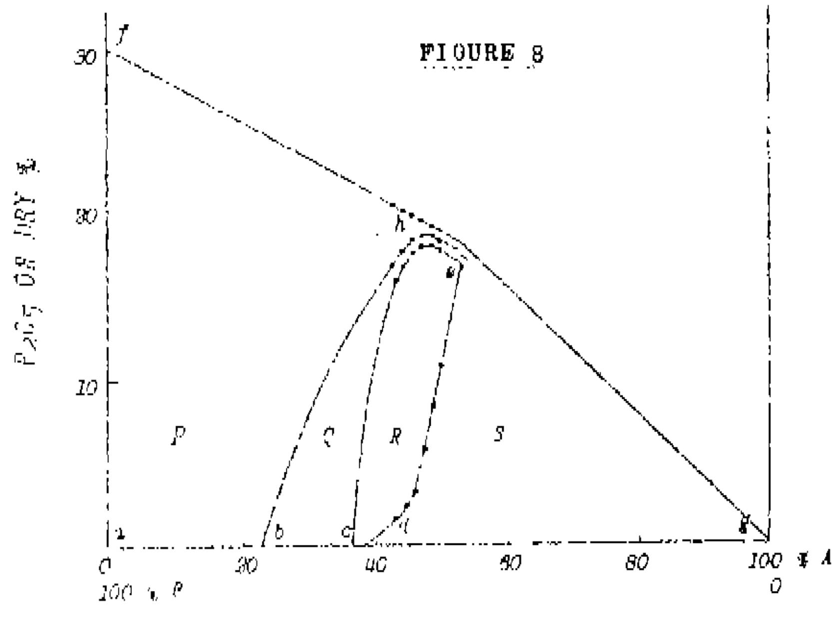


FIG. 7.



o Three days after preparation.

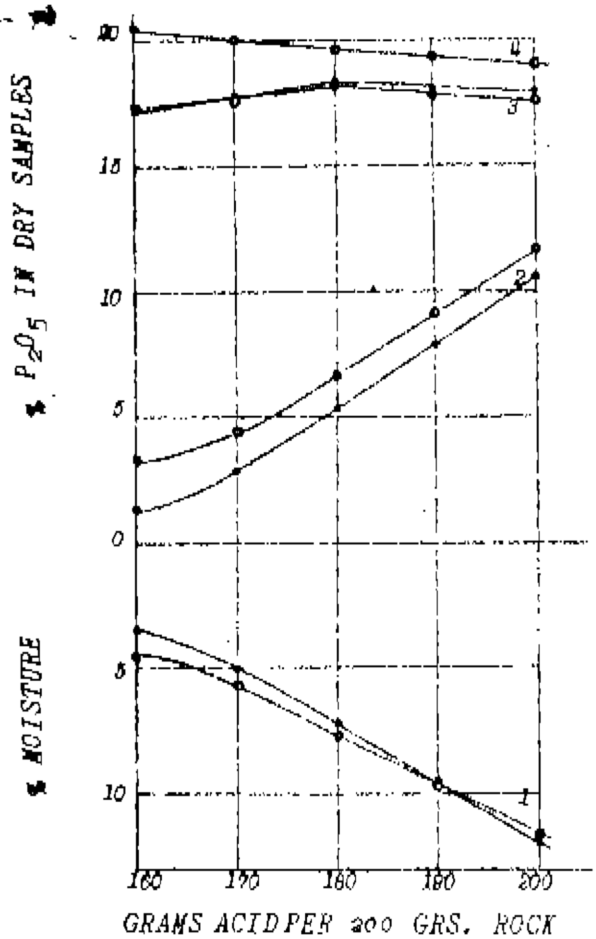


FIG. 1.

1. Moisture curves.
2. Free acidity curves.
3. Water soluble P_3O_5 curves.
4. Total P_2O_5 curve.
o Three days after preparation
• After 30 days ageing.

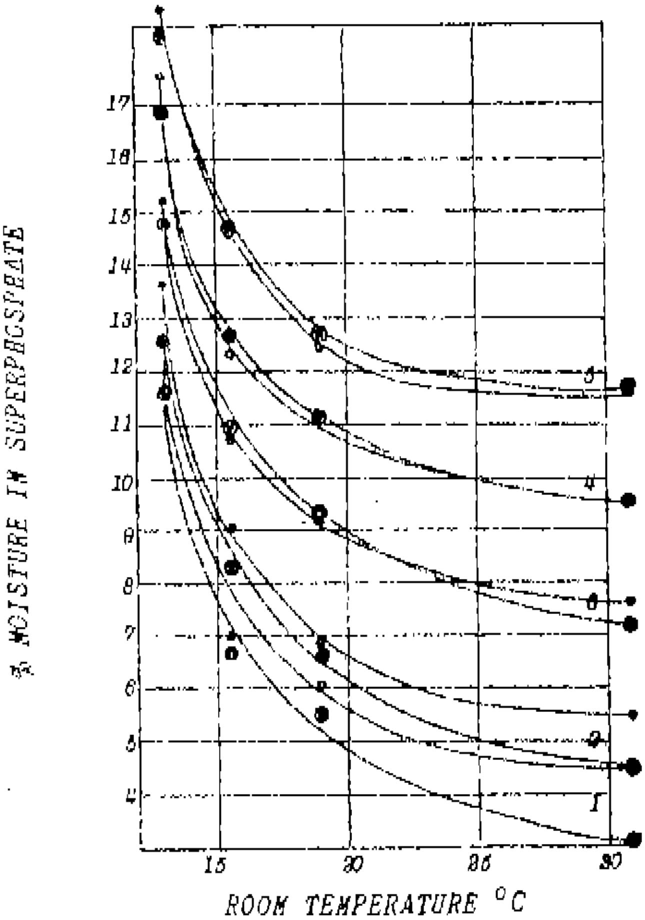


FIG. 2.

1. 1-5 Curves for samples containing rising amounts of acid.

o 3 days after preparation
⊕ after 30 days ageing.

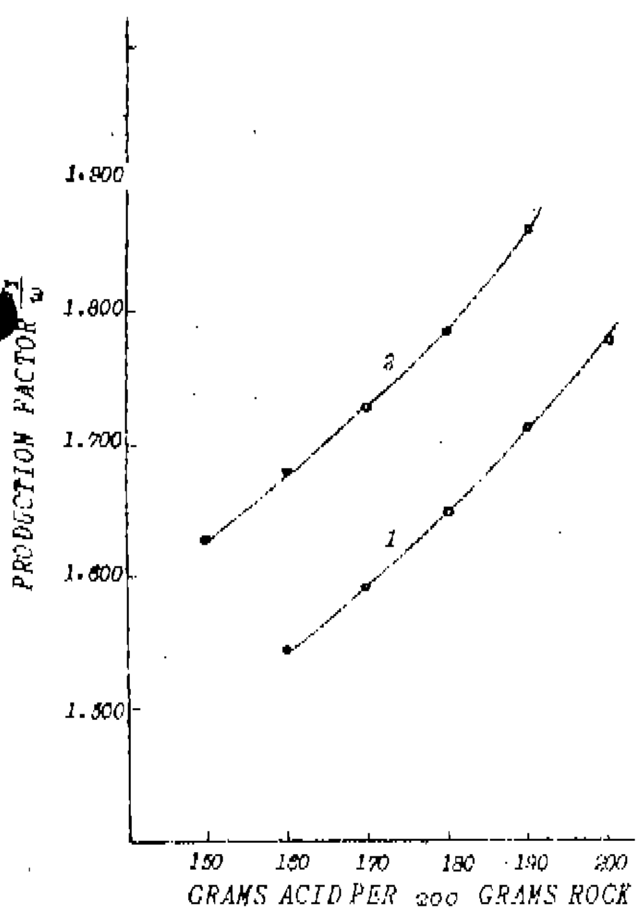


FIG. 3.

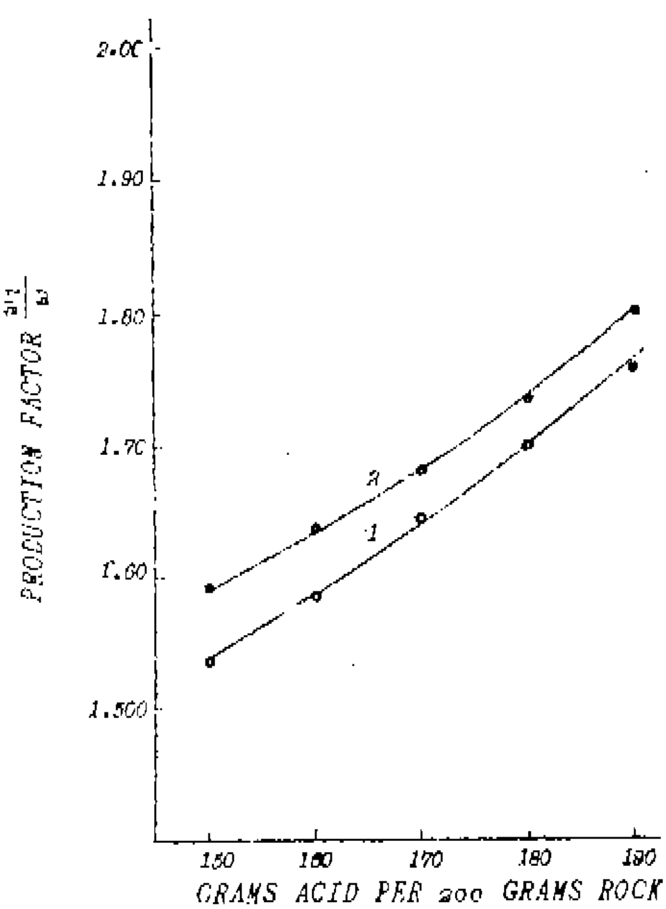
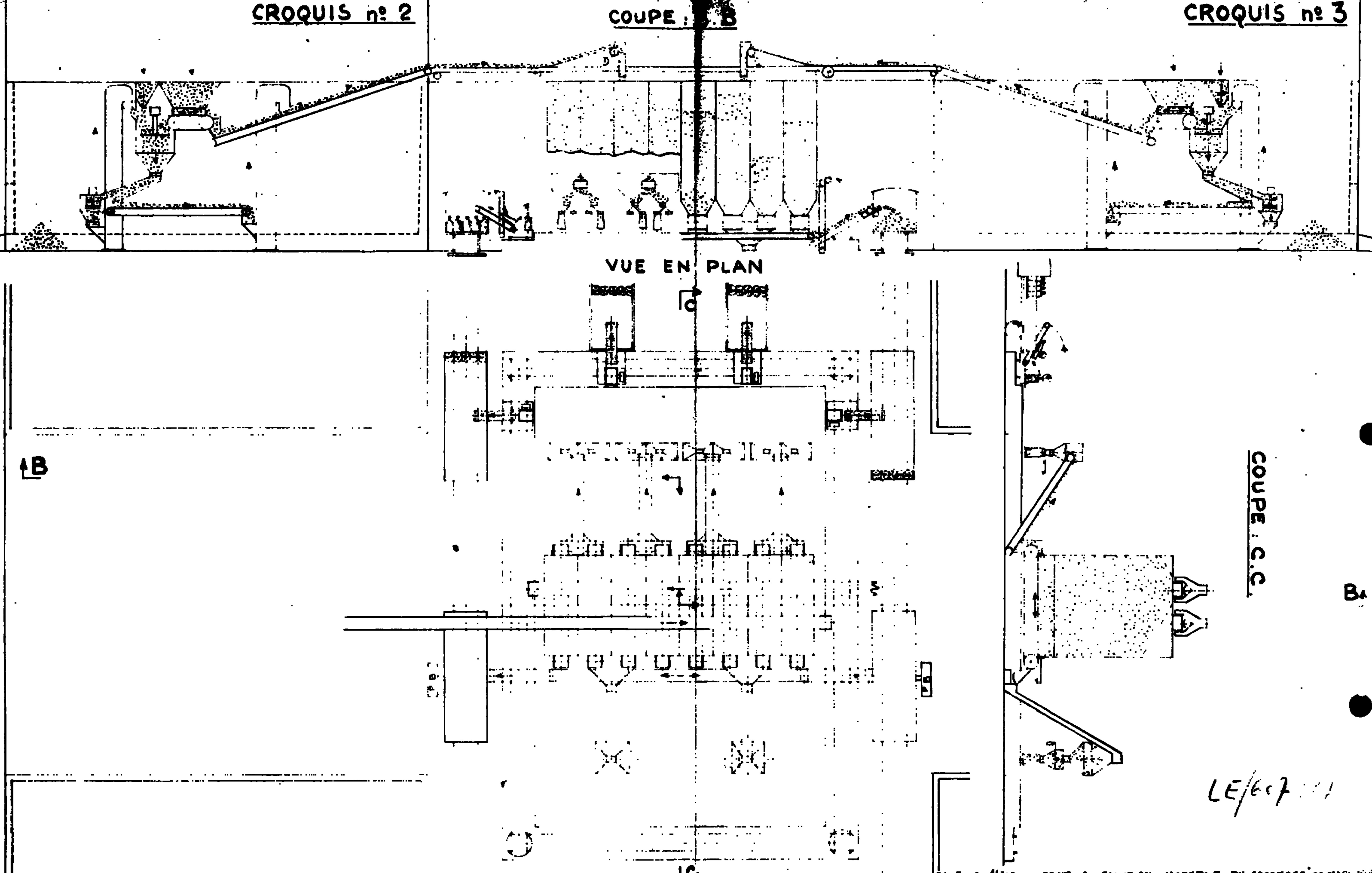


FIG. 4



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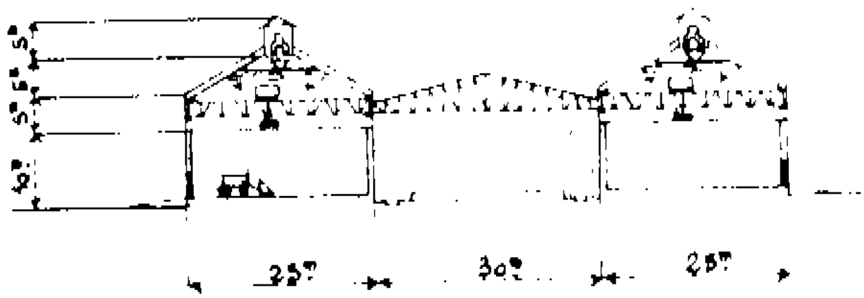

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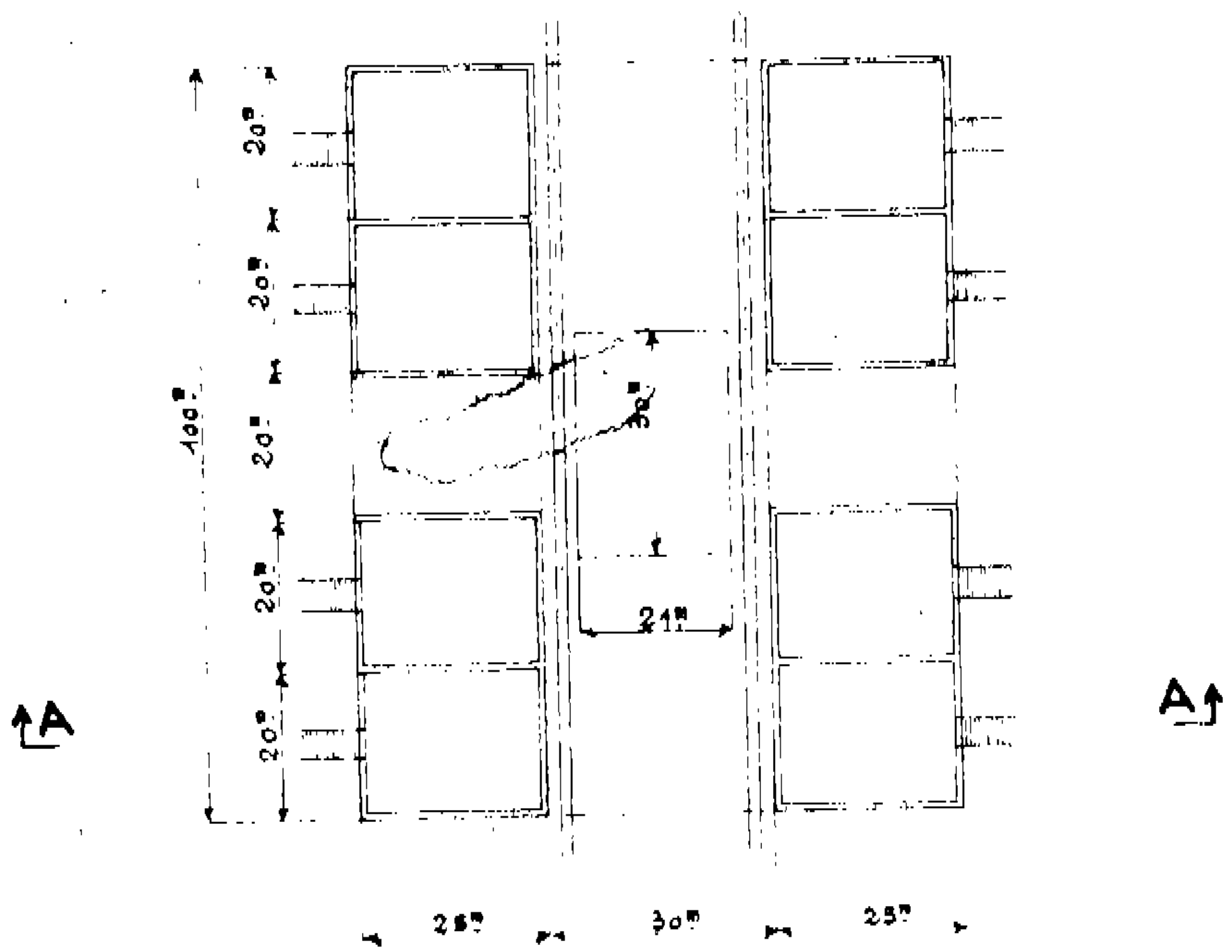

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