

Extraction of Magnesium From Dolomite-Rich Phosphate Rock

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As the high grade deposits of phosphate rock in Florida are depleted, future sources of P_2O_5 for Florida Producers will be derived from lower grade ores. These lower grade ores are sufficiently different from the high grade phosphate rock presently being processed such that major changes in the processing may be required in order that acceptable P_2O_5 yields can be achieved and an acceptable quality of phosphate products maintained. Processing to remove MgO , CO_2 , Fe_2O_3 , and Al_2O_3 in the lower grade rock prior to acidulation will be necessary because these impurities cause both processing problems and degradation of product quality. If these problems are not overcome, domestic phosphate producers will face difficulties meeting competition (1,2).

Magnesium is probably the most serious impurity in the phosphate rock from the southern Bone Valley Formation. It is frequently present as a dolomite mineral that is partially encapsulated within the phosphate rock matrix (2,3,4). Undesirable $MgCO_3$ in the phosphate concentrates can:

- interfere with the processing of the phosphate rock by reducing the rate of P_2O_5 production.
- interfere with the filtration of the gypsum by-product.
- carry through the processing to become a serious impurity in the diammonium phosphate (DAP) product (lowers nitrogen content in DAP).

- precipitate an insoluble magnesium salt in the phosphoric acid during storage and shipping (creates handling problems and lowers P_2O_5 content).
- increase sulfuric acid consumption.
- increase defoaming requirements.

Resolution of the problems arising from the presence of excessive levels of magnesium in phosphate rock and subsequently in the phosphoric acid have followed along three approaches. The most commonly used approach involves the selective mining of low magnesium phosphate rock coupled with flotation techniques to beneficiate the P_2O_5 levels while reducing the MgO in the phosphate rock concentrate to acceptable levels. Studies of the fatty acid-fuel oil flotation beneficiation of the magnesium rich phosphate from southern Florida by Llewellyn et al. (2) and Rule et al. (3) and Lawver et al. (4) have shown that the separation of the dolomite from the phosphorite is hampered by the dolomite/phosphorite rock matrix and by the similar flotation properties of the carbonates and phosphates. Stowasser (1) has compiled statistics for the industry that show nearly 1/3 of the P_2O_5 content of the ore is lost during beneficiation.

The second approach to avoiding the problems due to magnesium in the phosphate rock relies upon a chemical leaching pretreatment of the ore in order to remove many of the impurities prior to acidulation has been reviewed by Kouloheris (5). The use of weak acids such as aqueous sulfur dioxide to selectively leach magnesium from the dolomite component in south Florida phosphate concentrate was evaluated by Hansen et al. (6). Aqueous sulfur dioxide was found to leach the magnesia from the phosphate rock to levels around 0.5% MgO remaining in the phosphate rock. The remaining magnesium was believed to be bound to the phosphate as a mineral other than dolomite. Rule and others (7) investigated the aqueous leaching of low MgO phosphate rock by ammonium sulfate, dilute sulfuric acid, and sulfur dioxide. They found that dilute sulfuric acid reduced MgO content to less than 0.1% MgO with P_2O_5 losses of 6%. Treatment of the rock with ammonium sulfate was only able to drop the MgO content to 0.3%. Their ammonium sulfate

system required the phosphate rock to be roasted at 900°C, and leached at 100°C using a high concentration of ammonium sulfate. Aqueous sulfur dioxide was observed to remove MgO to less than 0.1% MgO without loss of phosphate.

A third approach to the magnesia problem is based upon purification of the acid after acidulation of high magnesium bearing phosphate rock. One technique utilizes a digestion of the phosphate rock with a crude phosphoric acid to form a soluble intermediate calcium acid phosphate (8). Purification of the soluble calcium acid phosphate takes place during the digestion and the purified phosphoric acid is recovered by further treatment with sulfuric acid to precipitate the calcium. This approach requires two filtration steps and only offers a slight improvement in phosphoric acid purity. Magnesium still remains as a problem. An ion exchange treatment of the dilute phosphoric acid to remove magnesium and other impurities results in an improved quality of the phosphoric acid products, but the problems associated with the magnesium and other carbonate impurities in the acidulation processing of the phosphate rock are not resolved. Several fixed bed ion exchange processes have shown promising results in the purification of the phosphoric acid product from the acidulation of high magnesium phosphate rock (9), however, these approaches appear to either introduce a new set of problems or only handle some of the minor aspects of the magnesia impurity problem.

This research was intended to satisfy three specific objectives:

1. To develop a method for quantitative leaching of magnesium from phosphate rock to levels less than 0.3% as MgO.
2. To identify and leach other impurities in the phosphate rock that could become problems during acidulation or become impurities in the phosphoric acid products.
3. To identify and isolate magnesium chemical by-products from this pretreatment of the rock or concentrate.

Results and Discussion

This process for magnesium extraction from phosphate ore has three loops. It was developed at the University of South Florida

with the financial support of the Florida Institute of Phosphate Research. The first loop is a CO₂-based ion transfer leaching step resulting in the extraction of the carbonates of calcium and magnesium from the dolomitic phosphorite. The second step is a product recovery loop in which magnesium, calcium and other nuisance ions (excess iron, aluminum, etc.) present in phosphorite are also extracted by the process and useful products are produced. Depending upon the configuration of the second loop, recovered by-products would be magnesium hydroxide, calcium carbonate, and/or calcium-magnesium acetate. The third loop regenerates the ion exchange material while recovering both acid and ammonia consumed in the process as ammonium phosphate or ammonium sulfate. Overall, the second and third process loops act together as a two step regeneration of the ion exchange material. A schematic of the three loops of the process is shown in Figure 1.

In the first loop, the dolomite-rich size-classified phosphate rock is leached with carbon dioxide as the leaching acid. During the leaching, the leaching liquor is continuously treated by means of an ion exchange material to remove dissolved magnesium, calcium and other cations. This leaching is nearly complete in about 0.5 hour as long as calcium and magnesium concentrations in the leach liquor are maintained at low levels. Some fine particles are formed during leaching but the rock remains with initial particle size distribution nearly intact. As the leaching action progresses toward completion as based upon the pH of the solution becoming constant, the treated rock is separated from the liquor/ ion exchange material and then exits the process.

Capabilities of the process will be illustrated by results of treatment of representative low-grade dolomite-rich phosphate rock samples. Low-grade phosphate rock feedstock compositions are summarized in Table 1. These feedstock samples would not be considered commercially useful for the composition shown. The treated phosphate rock compositions are shown in Table 2. Treated phosphate rock has commercially acceptable bone phosphate levels and much better magnesium and calcium levels. The molar ratio of calcium to P₂O₅ is much more satisfactory than most acidulation

feedstocks. The acid insolubles in the feed stock increase in proportion to the weight lost to the extraction to become one of the limiting factors in the improvement.

A materials balance for feedstock number 3 will serve to correlate the materials consumed in the process with products formed as a result of the treatment. This summary is shown in Table 3 for a basis of 1000 tons of dolomite-rich phosphate rock. For this comparison the losses due to ion exchange material are estimated. The ion exchange material quantities used for this treatment is based upon the following calculation:

$$R = \frac{W_R}{W_P} = \left[\frac{(M_{CaO} + M_{MgO})}{(M_{P_2O_5})} - X \right] M_{P_2O_5} \times (2/C_R)$$

where the symbols are defined as follows:

R - ratio of the weight of ion exchange resin to weight of phosphate rock

W_R - mass of resin in grams

W_P - mass of phosphate rock in grams

M_{CaO} - moles of CaO/100 g phosphate rock

M_{MgO} - moles of MgO/100 g phosphate rock

$M_{P_2O_5}$ - moles of P_2O_5 /100 g phosphate rock

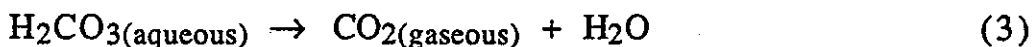
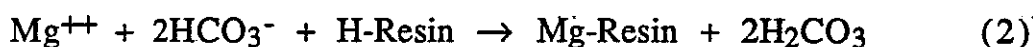
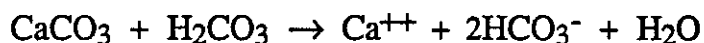
X - has the value of 3 for treated phosphate rock product having tricalcium phosphate as the source of P_2O_5 . A value of X between 1 and 3 is used to obtain a treated phosphate rock product having calcium acid phosphates as the source of P_2O_5 .

At this time relatively large quantities of ion exchange material are involved in the process, but this requirement is dependent upon both the capacity of the ion exchange material (3.4 meq/g) and the quality of the phosphate rock. The transfer of calcium and magnesium to the ion exchange resin is summarized in Table 3. These data suggest that the transfer is quantitative with respect to the capacity of the resin.

A relationship between the weight leached from the phosphate ore and the resin/rock ratio is shown in Figure 2. Selectivity favors calcium over magnesium throughout the range of ion transfer studied. These are summarized in Figure 3. Developments in our laboratory suggest that ion exchange materials having capacities 10-20 times that presently used for these data are possible. These developmental ion exchange materials are based upon ceramic structures. With these developments in mind, the materials input of ion exchange material would be considerably decreased (< 1T/1000T). Carbon dioxide is both an input and output material in this process.

When the stoichiometric dosage of ion exchange resin is used to treat phosphate rock to a CaO/P₂O₅ molar ratio of 3, there are more equilibria than simple acid-base acting in this system. Carbonic acid in water and the hydrogen-form cation exchange resin in deionized water each have an equilibrium pH near 3. Dolomitic phosphate rock in deionized water has an equilibrium pH near 8. After a stoichiometric ratio of an ion exchange resin slurry is mixed with phosphate rock slurry, the resultant pH is observed to be near 1.5. This relationship can be observed from the data presented in Figure 4. This complex equilibrium appears to be related to the carbon dioxide solubility because additional solids precipitate as the carbon dioxide is released from the leaching liquor upon standing. Evolution of carbon dioxide from the reaction is shown in Figure 5. These observations can be explained by the following reactions describing carbonation in ion transfer.

$$1.5 < \text{pH} < 3$$



If reaction (3) is slow to reach equilibrium, the carbon dioxide would buildup in the leach liquor such that reactions (1) and (2) are dominant. Since carbonic acid only partly dissociates in water, high levels of carbonic acid in solution are necessary to account for the low pH's observed in the process. A slow approach to equilibrium for reactions (1) and (2) permit this build up to happen. Traditionally, in order to overcome the limitations imposed by reaction (3) in systems without an ion exchange resin present (reactions in (2) are not present) high carbon dioxide pressure over the leaching reaction is necessary in order to gain enough solubility of carbon dioxide (Henry's Law Relationship) to push reactions in (1) toward solubilization of the magnesium and calcium carbonates. The original approach to buffered leaching was based upon increasing the solubility of carbon dioxide and improving the approach to equilibrium of reaction (3). The ammonium ion stabilized the bicarbonate ion rather than carbonic acid.

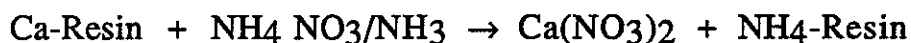
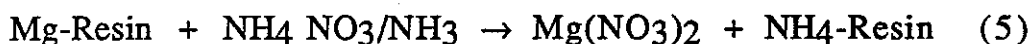
These equilibria suggest that an approach that increases the rate of solubilization or maintains equilibrium concentrations of carbon dioxide may be the key to carbonation based leaching of magnesium and calcium carbonates. Evidence already exists to support this interpretation. The observed $\text{CaO}/\text{P}_2\text{O}_5$ molar ratio below 3 in ion transfer leaching appears to be due to carbonation carried beyond the level supported by the ion exchange resin. Seawater contains an enzyme that allows the calcium and carbonate concentrations to exceed solubility equilibrium. Therefore, an enzyme represents one alternative to enhance carbonation based leaching. Another possible alternative includes catalytic adsorption of carbon dioxide (either heterogeneous or homogeneous) as a means to increase the available carbonic acid in solution to promote the reactions in (1).

Magnesium and calcium products are recovered as part of a two step regeneration of the ion exchange material. Ammonium acetate or ammonium nitrate solution is used to displace the magnesium and calcium from the ion exchange material to form a calcium-magnesium acetate or nitrate brine. Ammonium ion is

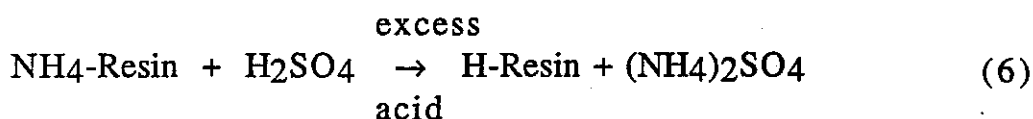
loaded onto the resin by this treatment. The resultant brine can be further worked up to give magnesium hydroxide, or magnesium carbonate, and calcium carbonate as products. Other product options are also favorable.

Restoration of the ion exchange material to the hydrogen form is carried out in the third process loop in which the ammonium form is converted to hydrogen form by treatment with phosphoric or sulfuric acids. Another by-product is formed by the combination of ammonium ion with excess phosphoric acid. As a result the ammonia and phosphoric acid consumed in the process are recovered as a valuable by-product.

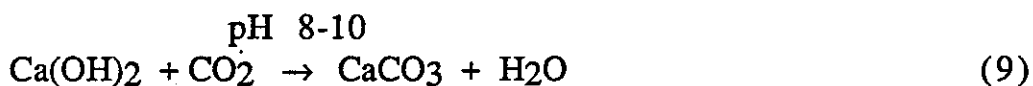
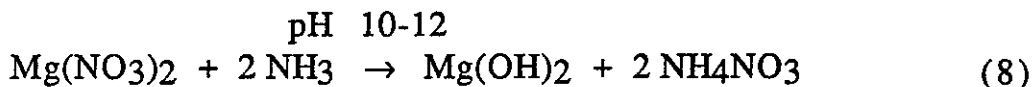
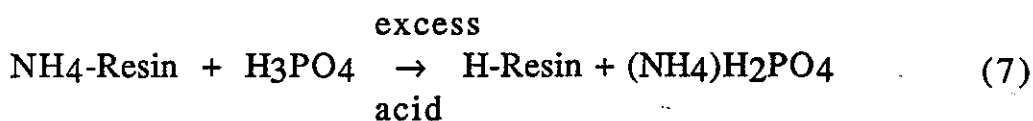
Step 1:



Step 2:



OR



As a pretreatment step to acidulation this process provides a means to a higher quality phosphate rock or pebble that is not presently available. Specifically, the carbonates of magnesium and calcium are removed before acidulation of the phosphate pebble or rock, thus avoiding many of the problems encountered in conventional fertilizer production. The pretreatment process

provides three advantages over conventional phosphoric acid production without pretreatment. These advantages are as follows:

- Upgrades phosphate pebble not presently suitable for fertilizer production to acceptable levels, thus extending reserves of phosphate rock.
- Provides by-products that have commercial value rather than becoming part of the acidulation process waste (e.g. gypsum).
- Produces a pretreated phosphate pebble that has should have distinct advantages over untreated phosphate pebble in the acidulation process steps.

Additional benefits due to this pretreatment process step extend into the products and wastes from the acidulation process step. Extraction of the calcium carbonate from the phosphate rock prior to acidulation reduces consumption of sulfuric acid, forms less gypsum waste, avoids water consumption in formation of the gypsum waste and reduces foaming from carbon dioxide evolution. Extraction of the magnesium carbonate prior to acidulation avoids problems in both the acidulation process and subsequent products. Magnesium stays with the phosphoric acid and strongly increases viscosity. Also, magnesium forms precipitates in phosphate products that limits product quality. We believe that the three loop process, properly developed, will be useful to the Florida Phosphate Industry and has even broader implications.

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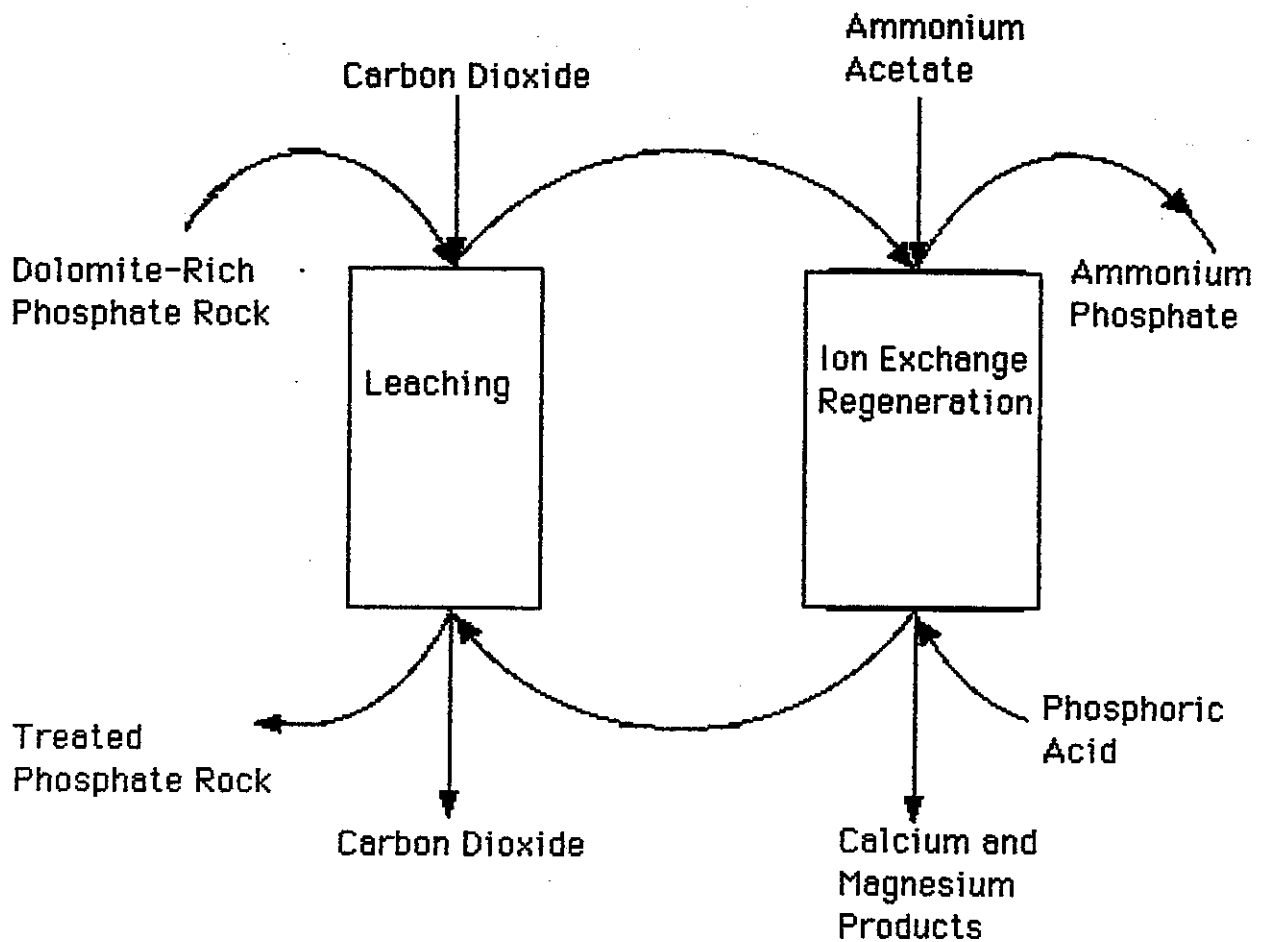


Figure 1. Schematic representation of the three loops of the Ion Transfer Process.

Table 1. Composition of Phosphate Rock Feedstock

Feedstock Sample Number and Mesh	Acid			
	Insolubles % w/w	MgO % w/w	CaO % w/w	P ₂ O ₅ % w/w
1. -18/+35	7.52	1.71	39.43	22.65
2. -35/+60	11.41	1.62	42.77	25.82
3. -60/+120	14.83	1.50	40.35	25.10
4. -120/+230	9.91	2.97	42.21	23.08
5. -230	4.98	4.43	44.07	21.05

Table 2. Composition of Treated Phosphate Pebble

Experiment	9/20	10/11	6/6	6/7
P ₂ O ₅ (% w/w)	29.36	25.39	23.50	28.59
BPL (% w/w)	64.2	55.5	51.3	62.5
BPL %	8.0	5.1	5.3	6.3
Improvement				
MgO (% w/w)	0.81	0.40	0.50	0.63
	-53	-87	-89	-63
MgO % Change				
CaO (% w/w)	27.1	28.1	32.0	29.9
	-31	-33	-27	-24
CaO % Change				
	2.3	2.7	3.4	2.6
CaO/P ₂ O ₅ (mol/mol)				

Table 3. Transfer of Calcium and Magnesium To Ion-Exchange Resin.

Experiment	Mole Ratio (Ca/Mg)	Moles Mg ⁺⁺	Moles Ca ⁺⁺	Resin Capacity (meq/gm)
817	7.4	0.0076	0.0562	2.56
913	11.3	0.0170	0.1920	3.96
914	11.5	0.0085	0.0980	4.10
922	9.2	0.0077	0.0706	3.08
101	10.9	0.0077	0.0843	3.67
1025 A	16.0	0.0025	0.0399	3.39
1011	12.2	0.0209	0.2569	2.77
066	5.9	0.0122	0.0722	3.37
067	11.7	0.0068	0.0798	3.44
1025B	10.7	0.0063	0.0675	3.00

Figure 2. ION TRANSFER LEACHING

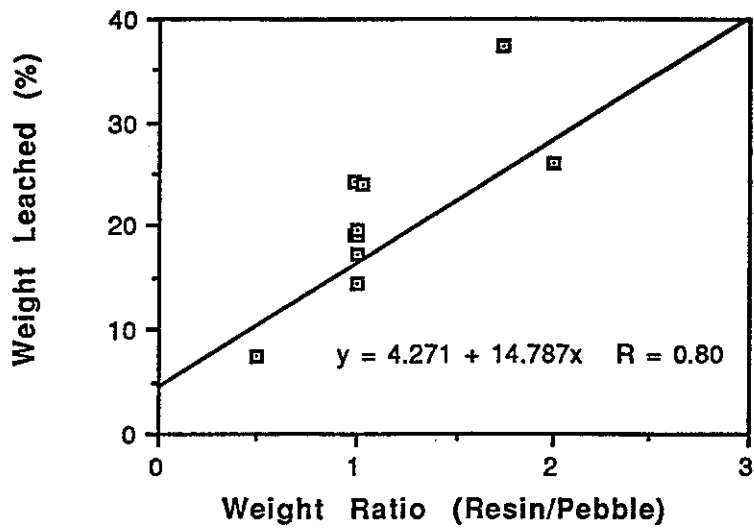


Figure 3.
Molar Ratio of Ion Transferred Calcium to Magnesium

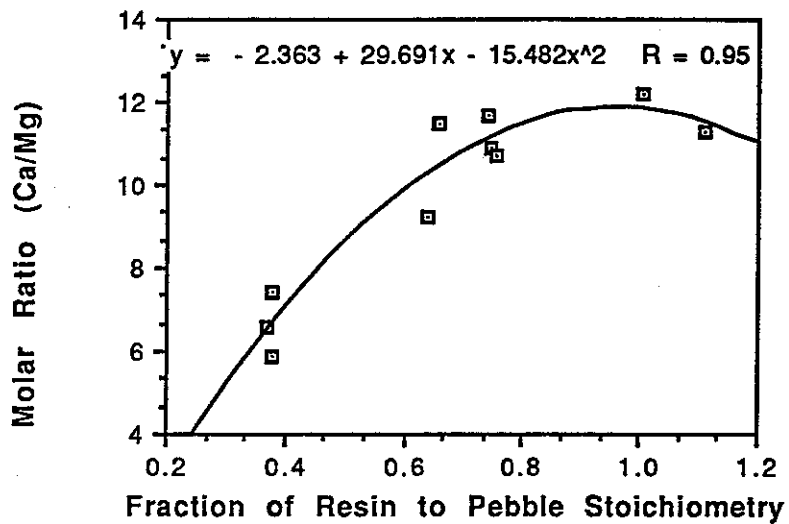


Figure 4. Rate of pH Change due to ion transfer.

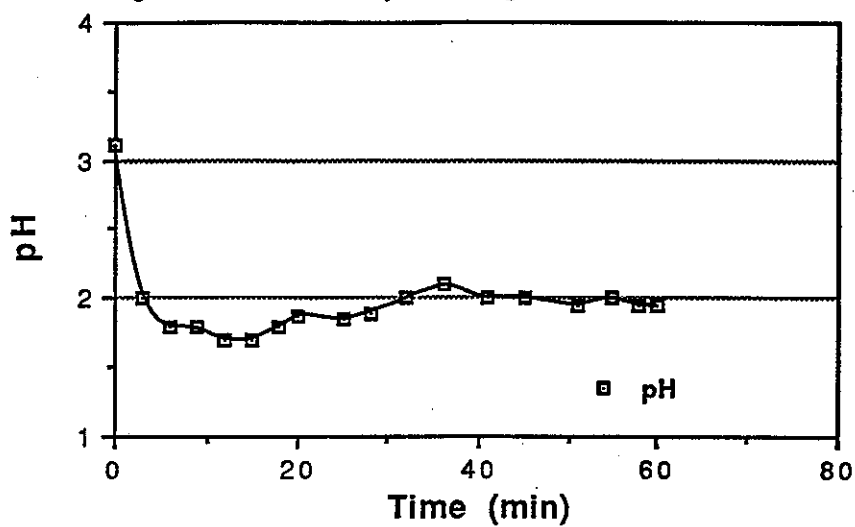


Figure 5. Evolution of carbon dioxide

