

A Study of the Interaction between Cement and Fatty Acids

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Introduction

Grinding aids may be described as products that improve the efficiency of the grinding process of cement when added to in small amounts. Amines, alcohols, fatty acids, lignosulphonates etc. have been empirically discovered as good grinding aids.

We can consider two main mechanisms for the action of grinding aids. These are based on the decrease in the resistance to comminution and on the prevention of agglomeration by shielding surface forces upon addition of a grinding aid. The former effect is based on the fact that grinding aids are adsorbed on the microcracks created by the mechanical stresses, eliminating or reducing their valency forces and therefore preventing microcracks from rejoining in the inactive period of mechanical stresses which act discontinuously during grinding. This effect depends on the diffusibility of grinding aids, since the grinding aid must reach and be adsorbed on the newly created microcracks before they may rejoin. If the microcracks are small compared to the molecular size of the grinding aids, their penetrability through the microcracks will also be effected.

When the ground grains have reached a given fineness, the surface forces on them reach such high values that the finest grains are forced to adhere to one another under the compression of the grinding media. By adsorbing grinding aids on the surfaces, we shield the surface forces in the ground material, thereby suppressing the agglomeration of the particles and providing conditions for higher grinding efficiency.

It has been reported that when the amount of triethanolamine added as a grinding aid increases, the fineness increases gradually at first. However, beyond a certain triethanolamine concentration, the fineness remains constant in laboratory cement grindings.¹ The optimum content of triethanolamine has been determined as slightly larger than that for a monolayer coverage of the cement surfaces.

In this report, we examine the interaction between cement and fatty acids, and using this

information, reinterpret the grinding data of cement with fatty acids previously reported.²

Experimental

The cement clinker used in these experiments was obtained from Canada Cement Lafarge Ltd. and ground to powder by using a shatter box. [In this paper, we will call it cement powder.] Its specific surface area (BET) was $1.47\text{m}^2/\text{g}$. The analyses were provided by the company and the oxide composition of the cement clinker used is given in table 1. There are five major oxides: calcium oxide (CaO), silicon dioxide (SiO_2), alumina (Al_2O_3), ferric oxide (Fe_2O_3) and magnesium oxide (MgO).

The samples were exposed to the vapour of the pure acid by enclosing a frozen sample of the acid in an evacuable glass chamber containing the cement sample. The acid had been previously degassed by several freeze-pump-thaw-cycles using liquid N_2 . The sample was degassed by evacuating the chamber before the frozen acid had thawed. After exposure for 2 days, the sample was evacuated for 1 day and then heated at 140°C , (at atmosphere), for 1 day. The weight gain of the samples due to absorption of the acid was measured by an analytical balance. Also, in another set of experiments, the weight gain of acetic acid as a function of exposure time was determined by observing the difference in the volume decrease of acid put in the evacuated chamber both with and without sample.

For FTIR measurements, a mixture of approximately 5% of cement powder in KBr was ground and pressed into a disc. The infrared spectra were taken with a Nicolet Model MX-1 FTIR spectrometer.

The specific surface area (BET) was determined by N_2 adsorption with a Quantachrome Sorption Analyzer, (Quantasorb Model).

Table 1. The oxide composition of the cement.

SiO_2	22.8%	Al_2O_3	5.53%	TiO_2	0.24%
P_2O_5	0.05	Fe_2O_3	2.84	CaO	64.2
MgO	2.63	Na_2O	0.22	K_2O	0.92
SO_3	1.17	LOI	0.07		

Results and Discussion

The percent weight increase of the sample after the acid had been exposed to the cement

for 2 days, (followed by 1 day of evacuation and 1 day of heating at 140°C), are summarized in table 2. In the case of acetic or propanoic acid, the sample weight increases by more than 100%. The percent weight increase generally decreased with longer chain length acids. For long chain acids, the percent weight increase of the sample was further increased with sample heating. With octanoic acid, for example, the weight increase is 1.0% at room temperature, while at 120°C it is 13.8%. It was assumed in these experiments that 2 days exposure to acid is enough to saturate the sample at any given temperature. For acetic acid, the reaction was completed after several hours exposure. The mass uptake as a function of time for acetic acid is shown in Fig. 1.

When the exposure was carried out with either acetic or propanoic acid at room temperature, a truly remarkable reaction took place, increasing the sample volume approximately ten fold. Likewise the specific surface area of the sample is increased. For acetic acid, the area increases from 1.47 to $39.50\text{m}^2/\text{g}$, i.e. a 27 fold increase. Even unground pieces of clinker exposed to acetic or propanoic acid vapour produced a dramatic increase in the specific surface area, with the clinker pieces being broken down to powder. The reaction took place more slowly, (from the surface to inside), than with ground cement. The specific surface area of a representative sample of unground clinker exposed to acetic acid was $24.1\text{m}^2/\text{g}$.

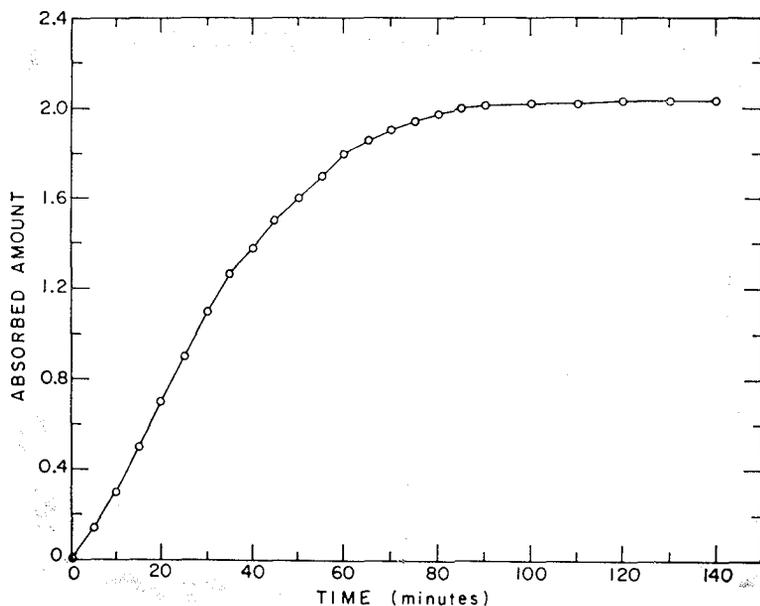


Fig. 1. The mass uptake of cement powder as a function of time for acetic acid.

The amount of acetic acid absorbed by cement corresponds almost exactly to two molecules of acetic acid absorbed per calcium ion in the sample. This implies the probable formation of $\text{Ca}(\text{CH}_3\text{COO})_2$. If all the Ca in the sample used becomes $\text{Ca}(\text{CH}_3\text{COO})_2$, a 134.9% sample weight increase is expected. This value is very close to the 129.2% measured. IR spectroscopy further corroborates the probable formation of $\text{Ca}(\text{CH}_3\text{COO})_2$ in the above reaction. The spectrum of the cement sample treated with acetic acid is quite similar to that of calcium acetate, which is prepared by neutralizing calcium oxide with acetic acid, followed by drying (fig. 2).

Only acetic and propanoic acids were taken up by the cement to the extent of approximately two acid molecules per calcium ion. Butanoic acid was absorbed to a lesser extent. The cement powder became gel-like during exposure to butanoic acid vapour for 4 days. Other acids used produced almost no volume increase, although all acids were absorbed to a considerable extent by the cement. Even for octanoic acid, the amount absorbed by the cement was very large compared to the amount required for monolayer coverage of the acid on the cement surface. The quantity of acid required for monolayer

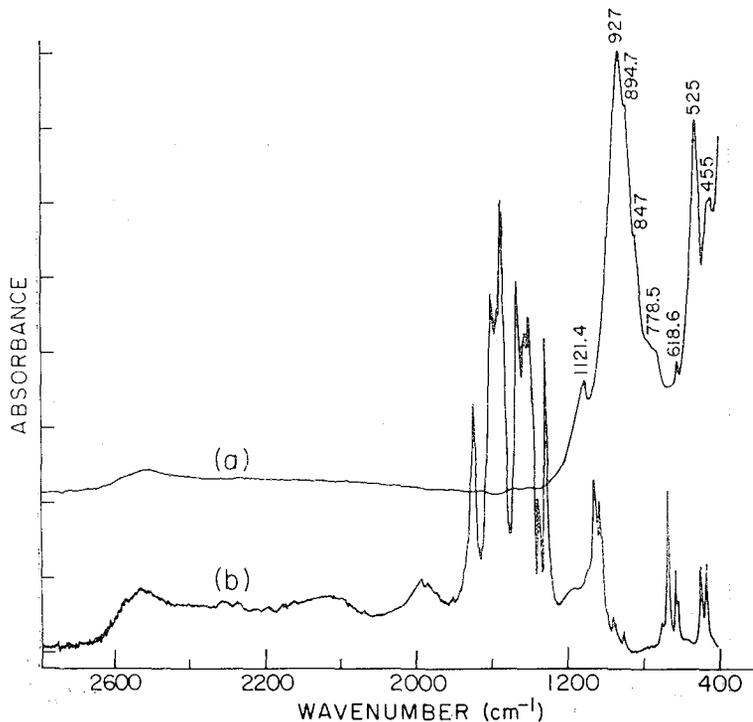


Fig. 2. The FTIR spectra of the cement powder (a) and that treated with acetic acid (b).

coverage was calculated by assuming the molecule to adsorb through the carboxyl group, with its alkyl tail projecting above the surface. It was also assumed that the entire surface would be uniformly covered with acid. In this case, the occupied area per the molecule would be similar to that of formic acid³ (13.4\AA^2) in the standing geometry. Using these assumptions, the quantity of octanoic acid that would be adsorbed to form a monolayer by a cement sample of specific surface area of $1.47\text{m}^2/\text{g}$ should be 0.25% of the weight of the sample. This value is smaller than the 1.0% actually measured at 22°C after the sample was evacuated for 1 day and heated for 1 day at 140°C to remove all the physisorbed acid from the cement surface. The large quantity of organic acids taken up by the cement may be understood in terms of the cement microstructure.

The crystal structure of tricalcium silicate which is the major phase in Portland cement, was determined by Jeffery.⁴ It has a $R\bar{3}m$ space group, and a structure composed of independent tetrahedra. The calcium ions link the tetrahedra, and are octahedrally coordinated to three ions which are not linked to Si^{4+} . The three octahedral holes per formula unit are large enough to accommodate other atoms and small molecules. Other phases of cement have similar holes in their structures. These holes are probably interconnected and form channels in cement. The acids most likely can penetrate the crystal lattice of the cement, provided the cross sectional area of the molecule is smaller than that of the channel. From Jeffery's work,⁴ one estimates that the channel is sufficiently large to accommodate acetic acid and propanoic acid. However, for large acids not all of their conformations of the acid molecules would have a sufficiently small cross section to allow immediate penetration of the cement by the acid. In particular, for long chain acids, ($\text{C}_6\sim\text{C}_{12}$), only the all-trans conformation would be capable of penetrating the cement, entering the fine pores in a snake-like manner. Consequently, with acetic and propanoic acids the penetration into the cement would be rapid, while for the longer acids the rate of penetration would be slow. There are 3 possible reasons for this slow penetration. First, the act of entering the pore would have to wait for the long acid molecule to adopt the rather improbable all-trans configuration. Secondly, when already within the pore, the transport of the bulkier long-chain acid would be more sluggish than that of acetic acid. A third impediment might also be imposed by a large acid molecule, having reacted with a calcium site. This could block access to the remainder of the pore. In contrast, acetic acid that might restrict the flow, once reacted with Ca, would not block it.

As a consequence of this, with for long-chain organic acids the number of calcium sites

that have reacted with two acid molecules, (and entirely breaking the previous Ca-O bond), would be very small, since it would be difficult to crowd the two acid molecules comfortably around the Ca ion in the pore. In contrast, acetic and propanoic acids are capable of achieving the desired 2:1 ratio. This may explain the observation that the reaction of cement with acetic and propanoic acids produces a large increase in specific surface area, (and simultaneous swelling), while the longer chain acids do not. In the former case, the Ca-O bonds that hold the cement structure together are totally broken, while in the latter they are not.

The molar saturation quantity of long chain acids was found to decrease with increasing chain length. This is probably due to the fact that, if one assumes that the long-chain acid can only penetrate the micro channels of the cement in the all-trans conformation, (i.e. with the hydrocarbon chain stretched out), then the longer the chain, the fewer the number of molecules that are required to fill the channels. This assumption can be made quantitative by using a simple model. Assume that V is the total volume of channel in a gram of cement, and A the cross-sectional area of the channel. If n molecules of acid of molecular length L completely fill the volume V , then:

$$V = nAL$$

Since for a given cement sample V is a constant

$$n \propto 1/L.$$

Thus, the number of molecules of long-chain acid needs to saturate a sample is inversely proportional to the molecular length of the acid. This is borne out experimentally. In table 2, the number of moles of acid taken up by the cement is given in the column B. In column C, a number is given which is proportional to the chain length, scaled so that it

Table 2. The percent weight of acids taken up by the cement.

Acids	A	B	C
Acetic	129.2%	2.15×10^{-2}	1
Propanoic	146.1	1.97×10^{-2}	0.75
Butanoic	55.0	0.62×10^{-2}	0.61
Pentanoic	53.2	0.52×10^{-2}	0.51
Hexanoic	47.6	0.41×10^{-2}	0.43
Octanoic	1.0 (22°C)		
	13.8 (120°C)		

A: wt% increase of the sample after the acid had been exposed to the cement for 2 days.

B: A divided by M.W. and 100. The unit is moles/g.

C: constant \times (1/chain length)

is unity for acetic acid. There is excellent correspondence between the data in columns B & C. The aforementioned proportionality is not expected for acetic and propanoic acids, since cement exposed to these acids has its entire structure destroyed, and the channels with it. Hence, the above analysis would no longer be applicable.

From the above data, we can calculate the channel volume and surface area. For hexanoic acid, the cross sectional area is assumed to be 13.4 \AA^2 (from formic acid data), and the length is calculated to be 8.84 \AA . Hence, the number of moles adsorbed on one gram of cement is $4.1 \times 10^{-3} \text{ moles/g}$. This corresponds to a volume for the channels of $0.29 \text{ cm}^3/\text{g}$, and a surface area of $2,832 \text{ m}^2/\text{g}$. The surface area of the channels is huge compared to the BET surface area, $1.47 \text{ m}^2/\text{g}$. Consequently, the surface area observed by the BET method does not include the area of the channels in the cement.

The FTIR spectrum of cement, obtained by the method given in the experimental section is dominated by SiO_4 vibrations⁵⁻⁷ at 455 , 525 and 927 cm^{-1} , (see Fig. 2). The strongest band is due to the ν_3 of SiO_4 at 927 cm^{-1} . The spectrum also indicates a small amount of SO_3 ($1,121.4 \text{ cm}^{-1}$) and a trace of hydrogen-bonded water ($\sim 3,400 \text{ cm}^{-1}$).

The FTIR spectrum of cement exposed to acid shows substantial differences (Fig. 2). In a sample exposed to acetic or propanoic acid for two hours, the band at 927 cm^{-1} has almost disappeared. Even in a sample exposed to acetic acid for 30 minutes, the intensity of this band decreased dramatically. The relative uptake of acid can be gauged from the ratio of the band near $1,600 \text{ cm}^{-1}$, due to acid, to the band at 927 cm^{-1} , due to cement. The $1,600 \text{ cm}^{-1}$ band was about 1.9, 1.4 and 1.3 times greater in the FTIR spectra of cement exposed for 15 hours to butanoic, valeric and hexanoic acids, respectively (Fig. 3).

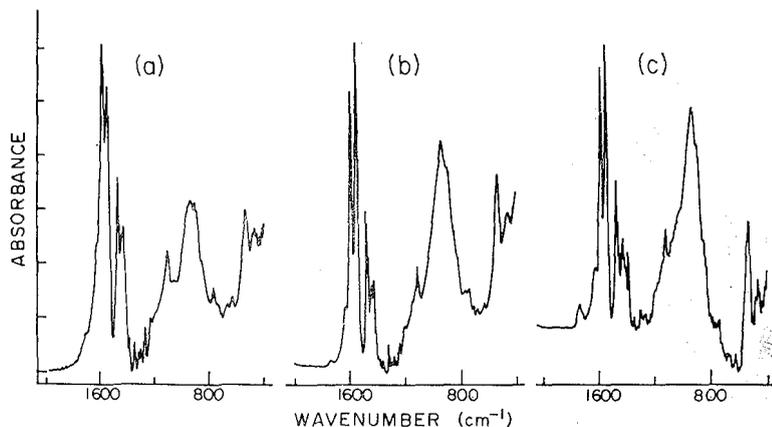


Fig. 3. The FTIR spectra of cement powder treated with butanoic acid (A), with pentanoic acid (B), and with hexanoic acid (C), respectively.

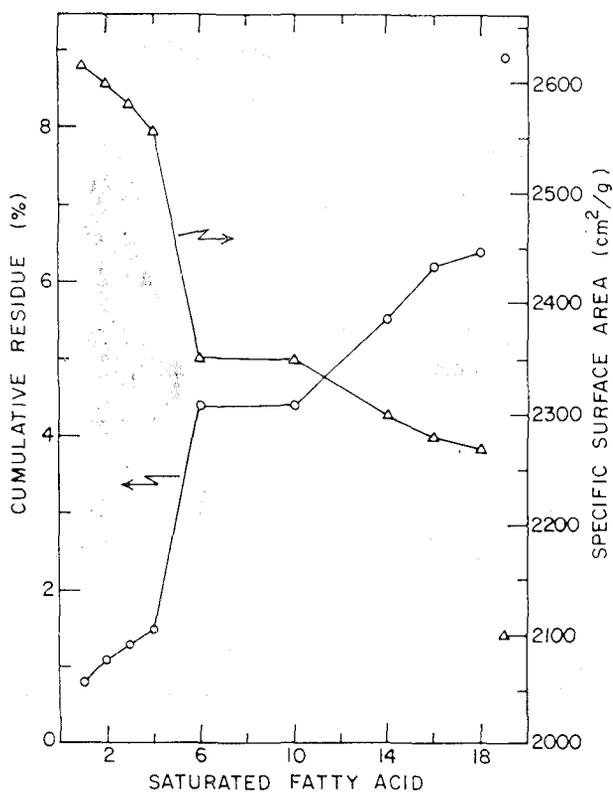


Fig. 4. Grinding efficiency of organic acids. The data was taken from reference 2. The most right data in graph are for no addition of acid.

The ratio between bands changed with the exposure time of the acid. For example, this ratio of $1,600\text{cm}^{-1}$ to 927cm^{-1} bands was very large for the sample exposed to butanoic acid for 4 days. It was also extremely large for acetic or propanoic acid.

There is an intriguing connection between IR data and the efficiency of these acids as grinding aids. It should be noted that acetic acid is used as a grinding aid and, in fact, is the substance of choice in grinding limestone. The efficiency of organic acids as a grinding aids is shown in Fig. 4. This is indicated by both the cumulative residue on 0085 sieve (the greater the residue the poorer the grinding aid) and as a specific surface area (the greater the area the better the grinding aid). The data was taken from a paper published by A.N. Gratschjan et al.² Note the sudden decrease in grinding efficiency upon going from butanoic to hexanoic acids, (unfortunately the data for pentanoic acid was not included in their paper). However, neither the pK_a of these acids, nor their cross sectional

area, (i.e. their abilities to cover the cement particles), differ markedly. Therefore, it is important to find the reason of the sudden decrease in grinding efficiency. In Gratschjan's experiments, 0.1wt% of acid was used in each grinding. This amount is larger than that needed for monolayer coverage of any surface whose specific surface area is less than $2,600\text{cm}^2/\text{g}$. For monolayer coverage of a surface whose specific surface area is $2,600\text{cm}^2/\text{g}$, only approximately 0.04wt% of hexanoic acid is needed. Hence, the amount of acid used in each grinding was large enough to give monolayer coverage. Therefore, the shielding effect, which prevents the agglomeration of cement particles, would be the same for all the grindings. Under these experimental conditions, the decrease effect in the resistance to comminution of grinding aids adsorbed on microcracks will be very important.

It should be borne in mind that only chemistry or surface chemistry processes which can occur during the typical residence time in a grinding mill are important in this context. Therefore, the efficiency of acids as grinding aids is critically related their diffusibility and penetrability through the microcracks created by mechanical stresses. Small acids, like acetic or propanoic, have good diffusibility and penetrability. The sudden decrease in grinding efficiency experienced upon going from butanoic acid to hexanoic acid suggests that these acids have very different penetrabilities through the microcracks, since the diffusibility of these acids would decrease smoothly with increasing molecular weight. Assuming that the dimension of the microcracks is not very different that of the channels in cement, we can find evidence of the different penetrability of these acids via FTIR spectroscopy. We have already discussed the fact that the ratio of the band near $1,600\text{cm}^{-1}$, due to acid, to that at 927cm^{-1} , due to cement, in the FTIR spectra shows the relative amount of acid absorbed on cement. Therefore, this value is proportional to the relative penetrability of each acid through the channels of cement. There is a large difference between the value with butanoic acid (1.9) and that with pentanoic acid (1.4). The latter value is similar to the ratio found with hexanoic acid, (1.3). The trend of the ratio from butanoic to hexanoic acid exactly corresponds to the results for grinding efficiency. No dramatic difference is expected in the physical or chemical properties of butanoic and pentanoic acid. One possible cause for the lower ratio with pentanoic acid may be due to the molecular shape of the chains in the liquid or gas phase. Usually, a linear molecule whose molecular chain unit is longer than 5 makes a pseudo-ring, or coil, formation in the liquid or gas phase. This formation will make it more difficult for pentanoic acid to enter the channels or microcracks of cement in a snake-like manner

than for butanoic, propanoic or acetic acid, each of which has an almost linear conformation.

Although the penetration of acetic acid through the microcracks of cement is much faster than that of butanoic acid, their grinding efficiency is not very different (see Fig. 4). This probably means that the time from the creation of microcracks to rejoining is long enough for even butanoic acid to penetrate and be adsorbed in the microcracks. When the chain length of acid becomes bigger than certain size, the molecule is hard to penetrate through the microcracks.

Therefore, for big molecules, the effect of decrease in the resistance to comminution adsorbed on the microcracks of grinding aids is negligible. Consequently, only the shielding effect of grinding aids is available. In Fig. 4, the flat region between hexanoic and decanoic acid may correspond to this condition.

For long chain length acids, 0.1wt% of these acids may be not enough for monolayer coverages of the surfaces. Therefore, the degree of coating of the cement grain surfaces decreases as the molecular weight of acid increases in this condition. Consequently, the shielding effect decreases as the chain length of acid increases for the big molecules. For this reason, the grinding efficiency of the long chain fatty acids decreases as the chain length increases further than that of decanoic acid (see Fig. 4).

In the previous discussion, we discussed the chemical reaction between acetic or propanoic acid, and cement grains. It is not clear that how the chemical reaction will effect the grinding process. Anyway, even 0.1wt% of acid is a very small amount compared to the amount needed for complete chemical reaction ($\sim 130\%$ for the case of acetic acid). The most molecules of acid may react with cement grains in the beginning of grinding and be changed to stable products. Therefore, they can not contribute in the rest grinding process by chemical reaction but only they have the shielding effect remained on the cement surfaces.

Conclusion

Acetic and propanoic acids react with almost all the Ca in the cement and to form $\text{Ca}(\text{CH}_3\text{COO})_2$ and $\text{Ca}(\text{CH}_3\text{CH}_2\text{COO})_2$, respectively. For other acids, they penetrate into the channels of cement. The surface area observed by the BET method does not include the area of the channels in the cement. The penetrability of each acid through the channels of cement is related to the efficiency of these acids as grinding aids.

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요약

초산에서 옥탄산까지의 지방산과 시멘트의 상호작용을 시멘트가루를 산증기에 노출시킨 시료의 퍼센트 무게 증가, 표면적 그리고 FTIR 스펙트럼을 관측하여 연구하였다. 시멘트가루를 초산이나 프로판산 증기에 노출시켰을 때 시료의 부피, 표면적 그리고 무게가 크게 증가하였다. 초산과 프로판산은 시멘트의 모든 칼슘과 반응하여 $\text{Ca}(\text{CH}_3\text{COO})_2$ 와 $\text{Ca}(\text{CH}_3\text{CH}_2\text{COO})_2$ 를 각각 형성한다고 결론지어졌다. 다른산의 경우 시멘트에 흡수되는 양은 시멘트 표면에 일부자층으로 흡착하는데 필요한 양보다 더 많았다. 이것은 시멘트의 채널속으로 산들이 들어가기 때문이라 여겨진다. 헥산산이 시멘트에 흡수된 양으로부터 계산한 시멘트의 채널 부피와 표면적은 $0.29\text{cm}^3/\text{g}$ 과 $2,832\text{m}^2/\text{g}$ 이었다. 이 채널의 표면적은 BET 방법으로 측정된 값 $1.47\text{m}^2/\text{g}$ 에 비하여 월등히 크다. 각 산의 시멘트 채널 속으로의 상대적인 침투력을 FTIR 스펙트럼에서 산에 의하여 나타나는 $1,600\text{cm}^{-1}$ 밴드와 시멘트에 의하여 나타나는 927cm^{-1} 밴드의 강도 비율로 측정하였다. 각 지방산들의 시멘트 채널속으로의 침투력과 표면을 덮는 정도의 자료를 이용하여 A.N. Gratschjan 등이 보고한 지방산을 이용한 시멘트 클링커 분쇄 결과를 재 해석하였다.