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EFFECTS OF CARBON DIOXIDE ATTACK ON GEOTHERMAL CEMENT GROUTS

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ABSTRACT

Studies of carbonation of geothermal grouts have shown that the physical criteria recommended by the American Petroleum Institute do not apply for durability in CO₂-containing fluids. The high silica binders, normally considered desirable because of their high strengths and low permeability, become permeable when carbonated. This allows further attack on the grout, and if the fluids are undersaturated with CaCO₃, then rapid corrosion will occur. On the other hand, grouts which contain appreciable amounts of calcium hydroxide have proved the most durable in CO₂-containing fluids despite their low strengths and high permeability. This is due to an impermeable layer of calcium carbonate which forms on the outside of the sample preventing further penetration of reactant species. Unless this layer is corroded, no further attack occurs.

INTRODUCTION

In geothermal well cementing, the recommendations set out by the American Petroleum Institute [API] (API Task Group, 1976) have provided criteria by which to test and judge different cementing formulations. In long-term exposure to geothermal fluids at Cerro Prieto, Mexico (API Task Group, 1985), a clear pattern emerged showing that long-term durability was obtained with cements meeting the API recommendations and which contained high silica additions. Finely ground quartz was the form of silica normally added to provide CaO/SiO₂ ratios in the region 0.6 - 1.0. The binders formed at these ratios have proved to be temperature stable over long periods. These recommendations have proved suitable for the high-brine content fluids common in the U.S.A., where the main problem is likely to be Cl⁻ ion attack.

However, recent work (Milestone and others, 1986a) has shown that reliance on the API recommendations for grouts exposed to high CO₂-containing geothermal fluids can cause serious problems leading to grout failure. In the development of the Broadlands geothermal field, New Zealand, a number of cases have been encountered where corrosion of the well casings from the exterior, rather than attack on the interior, has led to failure and rupture of the casing. Studies of samples retrieved during well work-over, together with cement bond logs suggest that there is little grout remaining around the casings in a number of wells. This corrosion of both grout and casing is attributed to the presence of high CO₂-containing fluids which lie several hundred meters above the production zone (Hedenquest and others, 1985). Although the genesis of these fluids is still uncertain, it is thought to be caused by the condensation of steam and gases from the production zone under an impervious sedimentary layer cooled by an inflow of cold water.

Corrosion studies (Milestone and others, 1986a) of grouts meeting API recommendations for strength and permeability showed that severe corrosion occurred within several months when exposed to this CO₂-rich fluid. Studies conducted at Brookhaven National Laboratory (BNL) and Chemistry Division, DSIR, New Zealand have been undertaken to unravel the reasons behind this rapid corrosion and apparent contradiction of the API criteria.

EXPERIMENTAL PROCEDURE AND RESULTS

A series of samples of API Class H cement with varying amounts of added silica flour were cured at 150°C and 250°C in water for seven days. When tested, all samples met the API recommendations for compressive strength, and samples with greater than 20% silica met that for permeability. The other criteria such as thickening time and cement/steel bond were not investigated. As expected, the addition of silica did provide increased strength (figure 1) and decreased permeability (figure 2). However, when these samples were tested for their resistance to carbonation

by treatment in a CO₂-pressurized autoclave, an unusual pattern emerged, in direct contrast to that expected. Figure 3 records the depth of carbonation after two-weeks treatment in water to which a pressure of ~550 kPa (80 psi) CO₂ was applied. At 150°C, carbonation in samples with less than 20% added silica is limited to a very thin layer of calcite on the outside of the samples. Those with greater amounts of silica, despite the low initial permeability, exhibit substantial rims of aragonite, another form of calcium carbonate.

Attack at 250°C is greater although a similar pattern occurs. With low silica additions, a thin calcite layer is formed, but at higher silica content, the binders are partially resistant so that the rim visible when the samples are cut radially does not mark the true edge of carbonation. Partial carbonation occurs almost to the center of the samples, and there is an increase in permeability. Table 1 shows the permeability of sample cylinders measured before and after two weeks carbonation treatment. The permeability of the carbonated zone is calculated assuming that the permeability of the material inside the reaction rim remains unchanged and is plotted in Figure 2. Full experimental details will be presented elsewhere (Milestone and others, 1986b).

Table 1. Permeability of samples

	Before Carbonation		After Carbonation	Carbonated Zone
	%SiO ₂	mD	mD	mD
150°C	0	3.40	6.74	Low
	10	0.0243	0.0119	Low
	20	0.0004	0.00136	0.0997
	35	<0.0001	0.0248	0.630
	60	<0.0001	0.0451	0.241
	100	<0.0001	0.0220	0.063
250°C	0	17.7	17.5	Low
	10	1.48	1.46	Low
	20	0.059	0.0711	0.44
	35	0.027	0.0352	0.050
	60	0.0037	0.0104	0.019
	100	0.0043	0.0147	0.025

DISCUSSION

The reason for this pattern is explained by considering the chemistry of the cement binders rather than their physical properties. At low silica additions, i.e., high CaO/SiO₂ ratios, the grouts contain appreciable amounts of calcium hydroxide together with phases that are both weak and permeable. The strongest binding phases are obtained by adding additional silica which reacts with the calcium hydroxide reducing the pH of the grout as well as the permeability. When attack by a carbonating species occurs, either by CO₂ (aq) or HCO₃⁻, the durability is inversely related to both strength and permeability but correlates well with calcium hydroxide content (figure 3). One of the main reasons for this is that when calcium hydroxide is carbonated, it forms calcite which has an increase in volume of 17% over calcium hydroxide. This means that calcite formation from calcium hydroxide has the effect of blocking off the pores, reducing permeability to water and ionic species slowing further attack. Indeed, in the pure cement samples, CO₂ penetration after two weeks is less than 0.1 mm and represents a very thin skin surrounding the samples.

On the other hand, in the grouts with added silica greater than about 30%, there is no calcium hydroxide present in the grout so that attack occurs directly on the calcium silicate hydrate binder. This produces calcium carbonate which occupies considerably less volume than the binder with the result that the carbonated layer of grout is considerably more permeable, and further attack is enhanced. After only two weeks carbonation treatment, the depth of penetration is several millimeters.

As can be seen in Table 1, the permeability of samples containing more than 10% added silica increases. At 150°C, the change for the pure cement sample is probably due to growth of binder crystals. The increase for the other samples is assumed due solely to the carbonated rim, the calculated permeability of which is shown in Figure 2. While this is reasonable for the 150°C samples, it is not strictly true for the 250°C. Above 20% added silica, the samples tested at 250°C show very diffuse carbonation rims, the outer edges of which mark the region where total carbonation, measured by thermogravimetry, has occurred (Milestone and others, 1986b). From the diffuse rim inwards, a decreasing amount of

calcite is found and is shown by the partial carbonation curve in Figure 3. Because the calcium silicate binder formed at low CaO/SiO₂ ratios at 250°C is partially resistant to carbonation, a permeability gradient will be formed which decreases from the outer edge of the diffuse zone to the center. Thus, the values in Table 1 and Figure 2 will be only an approximation for permeability of the carbonated zone at 250°C. Figure 2 shows that permeability of the carbonated zone peaks about 35% added SiO₂ at 150°C and 20% at 250°C. For samples high in silica, there is a large amount of unreacted quartz present which acts as an inert impervious filler, which partly explains the drop in permeability noted. The increase in permeability of the binder will be considerably greater than that estimated for the zone as a whole. At 35% silica addition, no quartz is detected by XRD, so the values obtained at this addition should be close to that for the fully carbonated binder.

At 150°C, the permeability of the carbonated zone for samples with commonly used SiO₂ additions of 20-60% lie well above the API recommendation for permeability of 0.1 mD. The situation at 250° is complicated by the permeability gradient that develops, but clearly carbonation increases the permeability of the binder, particularly between 15 and 25% added silica. In actual downhole testing at Broadlands, full carbonation occurred within several months for samples with 30% added silica at both 160° and 260°C. Significant corrosion occurred at 160°C (Milestone and others, 1986a), particularly for samples with added silica.

IMPLICATIONS

Geothermal fluids contain varying amounts of dissolved CO₂, usually measured or expressed as HCO₃⁻. Experience in New Zealand has shown that estimations of the total dissolved CO₂ in deep fluids are often low due to difficulties of sampling at depth and pressure and loss of CO₂ as the sampler is returned to the surface. If CO₂ is present in low to medium amounts, then carbonation will be relatively slow and may not be noticed if attack due to Cl⁻ or SO₄⁼ ion is also occurring. In neutral or alkaline fluids, dissolution or corrosion of the calcium carbonate formed will

be slow so that further chemical attack will be dependent on the permeability of the grout after carbonation and the mobility of Cl^- or SO_4^{2-} ions. In fluids which are mildly acidic at temperature due to dissolved CO_2 or SO_2 , the calcium carbonate will dissolve and thus corrosion of the grout will occur providing a fresh surface for carbonation and subsequent corrosion. This has occurred at Broadlands where the fluids are mildly acidic due to the high concentration of dissolved CO_2 . Levels up to 10,000 ppm are common with Cl^- concentrations usually no greater than 1600 ppm and often much less. The deeper production fluid has higher Cl^- ion and lower dissolved CO_2 . In one well studied at Broadlands, 2-in. x 4-in. cylinders of grout had lost 60% of their volume in 9 months (Smith, 1983).

Even if corrosion due to CaCO_3 dissolution does not happen, problems due to Cl^- or SO_4^{2-} ion attack either on the grout or casing are likely. Increases in permeability of the carbonated zone of up to 40 times have been recorded for some grouts studied at Brookhaven. Thus grouts, which following initial curing easily meet the API limit for permeability, after carbonation can lie well above the limit which was designed for high brine fluids.

A further point to be noted is the effect if bentonite is added to the grout slurry. This is often done to allow extra water to be added to the slurry for density considerations or extra fluidity. It has been found (Milestone and others, 1986b) that the presence of bentonite enhances the formation of tobermorite normally considered one of the best binders in well cements, at least up to 180°C . Addition of bentonite stabilizes tobermorite so that it can be present in grouts up to 250°C when it only slowly converts to the high-temperature stable binders. While the effects of CO_2 attack on the various silicate binders will be presented in detail elsewhere, it should be noted that tobermorite is one of the least resistant phases to carbonation. Thus, grouts are unlikely to reach their full strength potential since carbonation will remove the ability of the grout to develop the high-temperature stable binders.

From these results, it would appear that the best compromise between strength and durability for grouts exposed to fluids containing high concentrations of CO_2 would be at ~15 to 20% silica flour additions. In this

range, there is sufficient Ca(OH)_2 present to form a protective calcite layer, the permeability is less than 0.1 mD and the compressive strength above 7 MPa. However, the durability of grouts containing large amounts of calcium hydroxide is questionable (Kalousek, 1952) and actual long-term downhole testing is required to establish the lifetime of such grouts. Tests of such grouts are underway in New Zealand.

CONCLUSIONS

While the API recommendations have proved suitable as criteria for selection of geothermal grouts exposed in high-salt concentrations, they are not suitable when high CO_2 concentrations are encountered. The high silica phases, which normally make the best binders, become permeable when carbonated. This can lead to rapid attack by species such as Cl^- or SO_4^{2-} ions so that the problems of carbonation may not be noticed in high brine concentrations, even though they contribute to the reduced durability.

The most resistant grouts to carbonation are those which contain appreciable amounts of calcium hydroxide since an impervious layer of calcite forms on the outside showing further attack. This is also likely to prevent attack by other species unless it is corroded away. The maximum durability of grouts in CO_2 -containing fluids would appear about 20% addition of silica rather than the more usual 35% or greater, although the long-term strength of Ca(OH)_2 -containing grouts is questionable, and samples need to be tested downhole to determine actual lifetimes.

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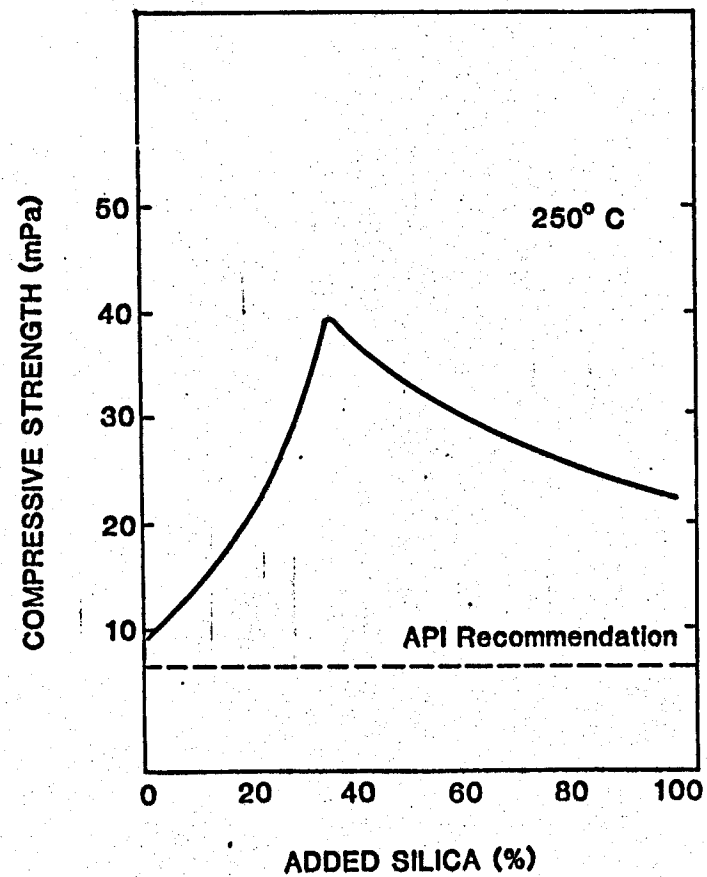
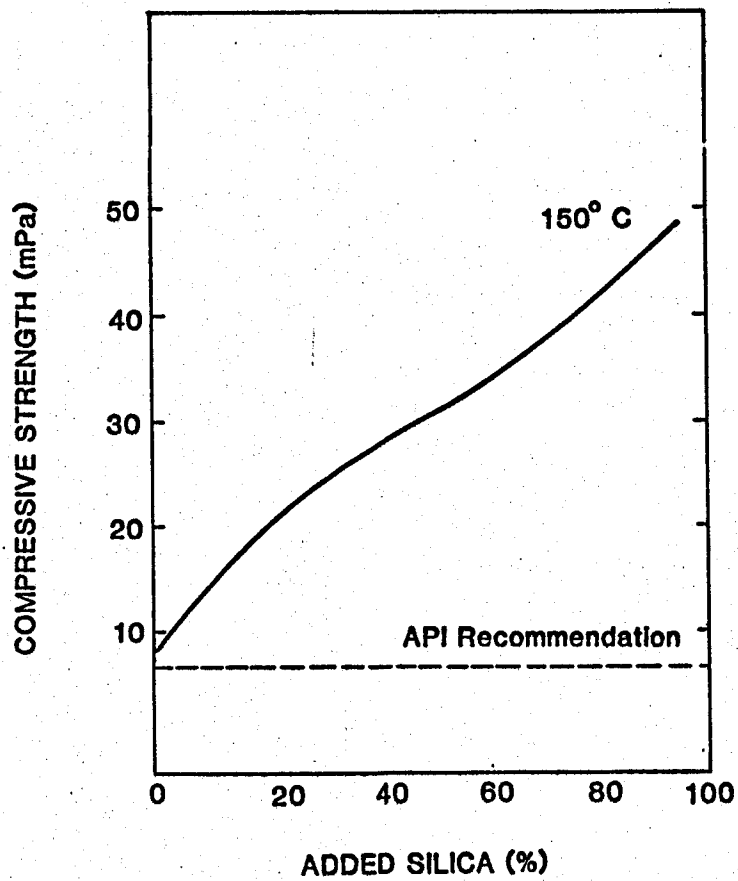


Figure 1. Compressive strengths of geothermal grouts.

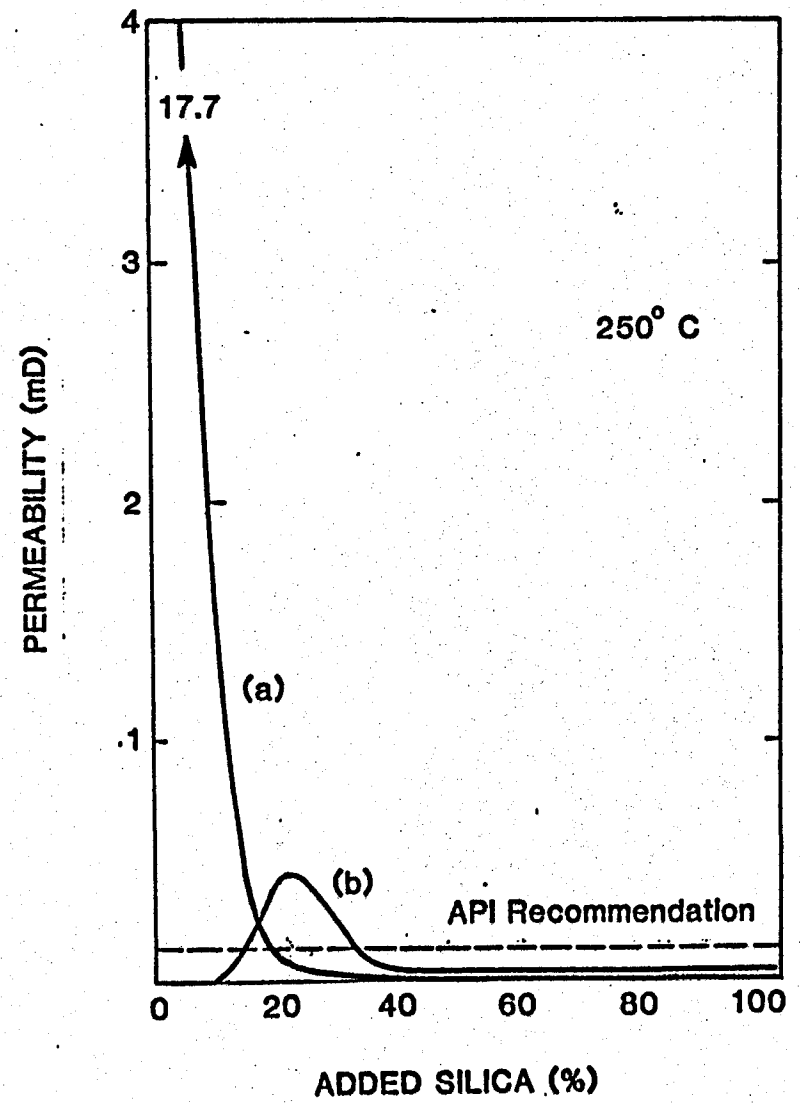
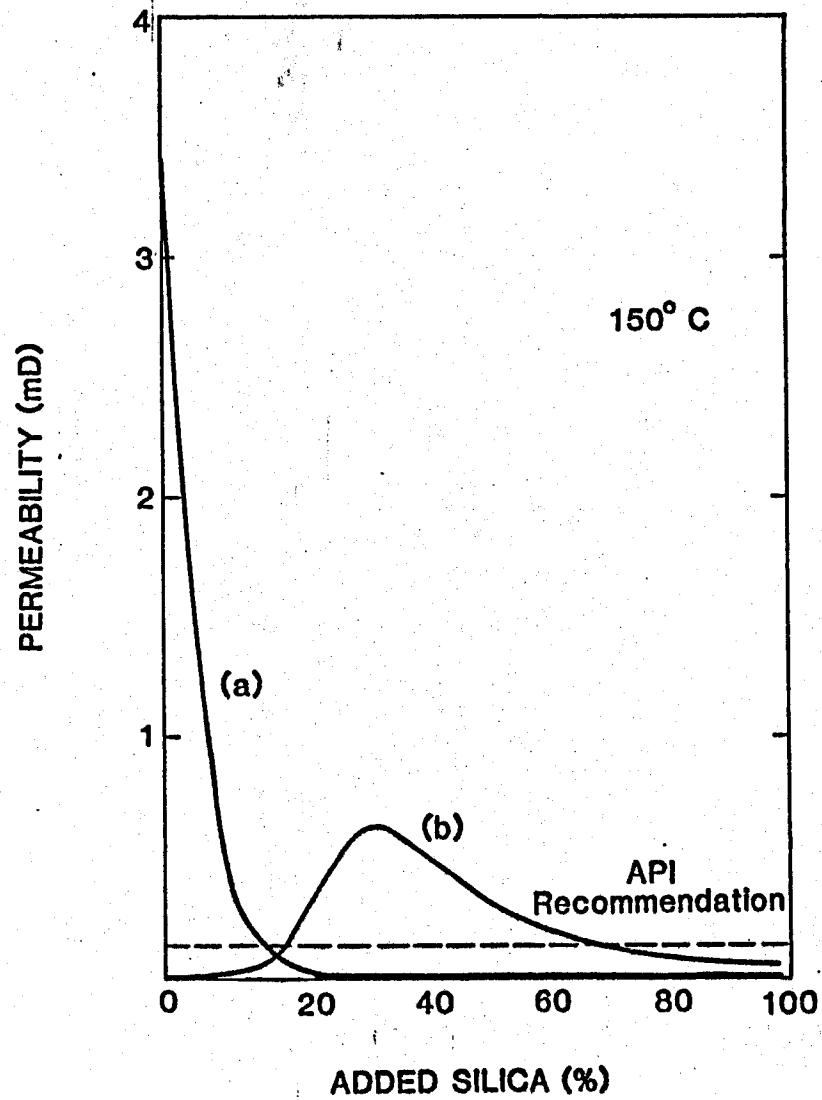


Figure 2. Permeability of geothermal grouts.
 (a) Unreacted sample.
 (b) Carbonated zone.

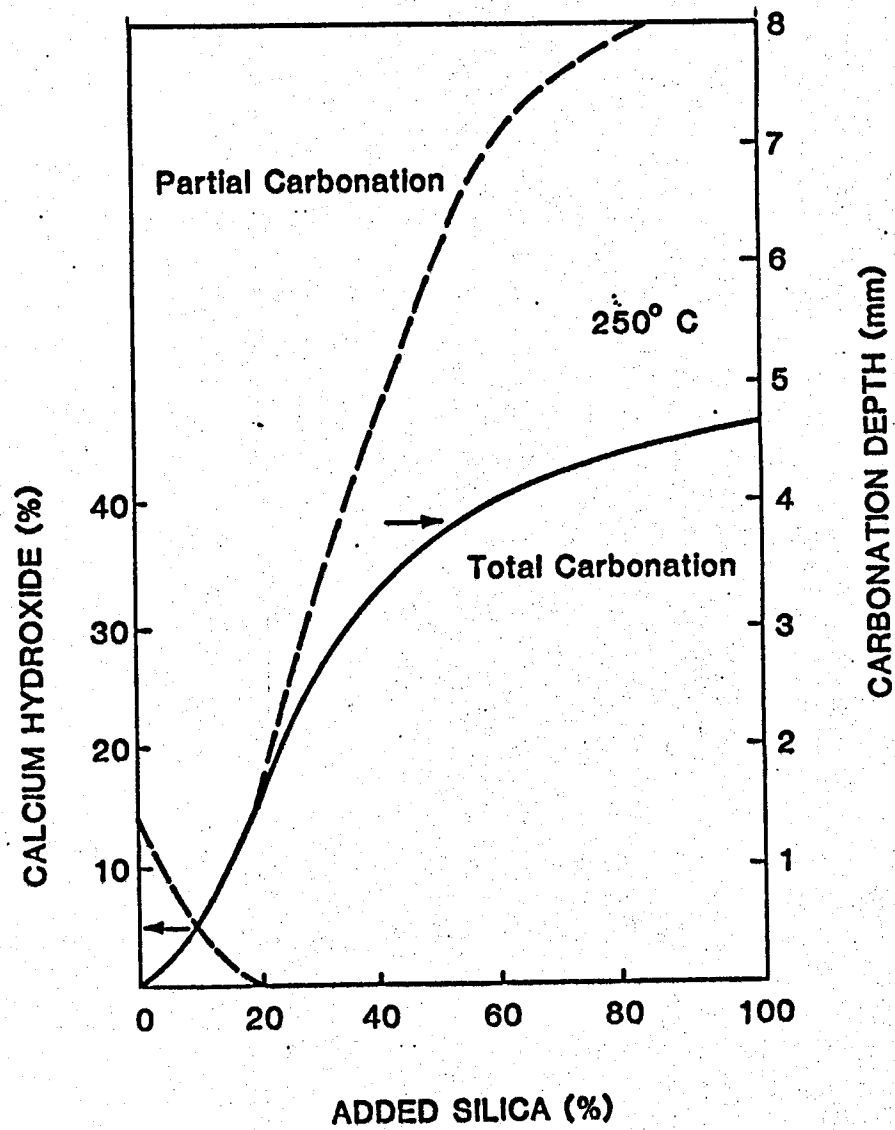
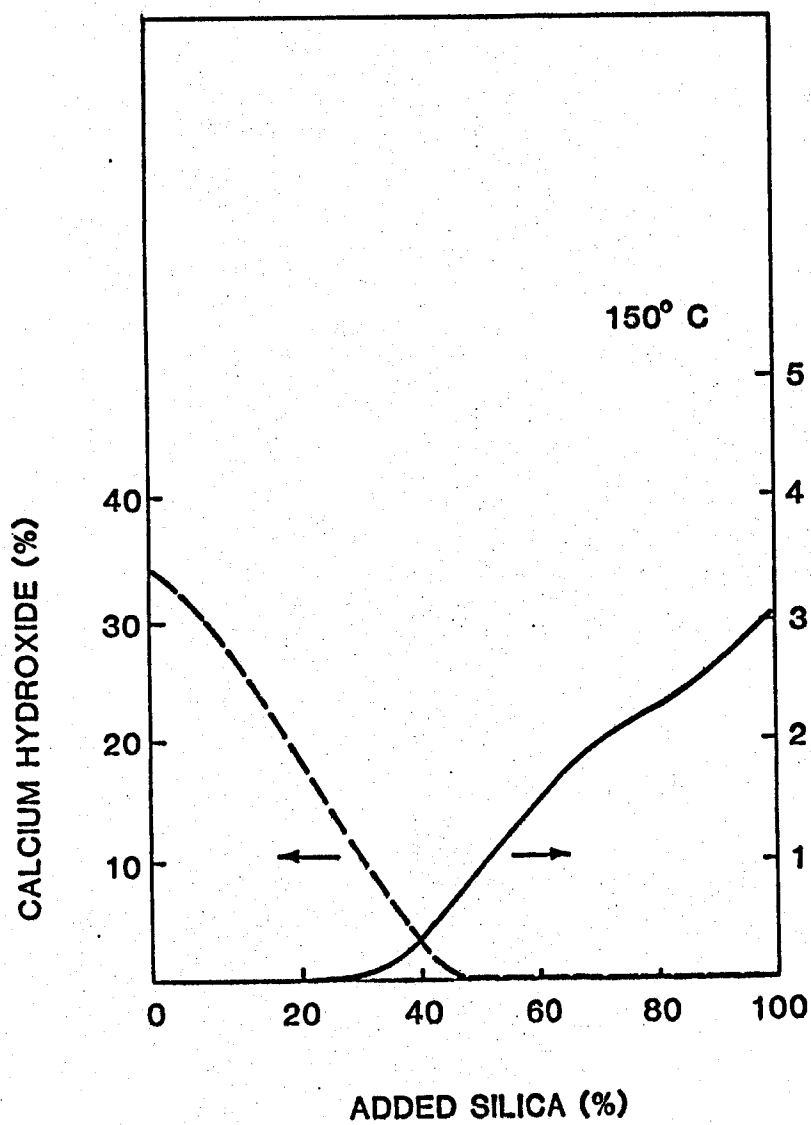


Figure 3. Depth of carbonation and calcium hydroxide content of geothermal grouts.