

## THE EFFECT OF MICROSILICA ON CARBONATION OF AIR-CURED FIBRE CEMENT.

LIN ZHEN<sup>1</sup> and HENNING M. THYGESEN<sup>2</sup>

<sup>1</sup>: *Elkem Materials Fibre Cement Lab, Jiandongyuan No.35, Chaoyang district, Beijing, P.R.China, lin.zhen@elkem.no*

<sup>2</sup>: *Cembrit Holding A/S, Sohngaardsholmsvej 2, DK-9000 Aalborg, Denmark, henning.thygesen@cembrit.com*

---

### ABSTRACT

Carbonation is inherent in cementbased materials, normally resulting in shrinkage. Uneven carbonation of fibre cement may lead to tension causing failure in the product, especially when fibre cement is installed in unventilated structures. Carbonation reaction in fibre cement products is influenced by several factors. Cembrit and Elkem decided to initiate a project to study the effect of microsilica (MS) on carbonation in air-cured sheets.

The following curing regimes were designed for this study: All the samples would be cured under the designed carbonation environment including dry-soaking stages for several months. This curing schedule is called a modified BAC schedule (“Beschleunigte Alterung mit CO<sub>2</sub>”). As a reference, another group of samples were cured simultaneously under “standard” condition without enhanced CO<sub>2</sub>. 3%, 5% and 10% microsilica were used in the recipes, and fine limestone was used as a filler.

Carbonation caused different influences on different properties of the final product.

Bending strength, moisture movement, water absorption and density were improved due to carbonation; however the bending work (toughness property) was visibly decreased, products becoming more brittle.

Shrinkage only increased in the samples containing 10% microsilica with 10% limestone after exposure to the CO<sub>2</sub> environment. There was no other visible result to indicate the shrinkage increased by adding microsilica, either when the sample was exposed to CO<sub>2</sub> or curing in standard condition.

Thermal gravimetric analysis (TGA) shows that the amount of CaCO<sub>3</sub> decreased with increasing dosage of microsilica, which means that the carbonation effect was reduced by adding MS.

There were no visible results in this test to show the properties of the fibre cement products were reduced due to using microsilica, or that negative carbonation effects were increased by adding microsilica.

### KEYWORDS:

Carbonation; microsilica; shrinkage

### EXPERIMENT

Test materials:

Microsilica was supplied by Elkem, and the other raw materials were supplied by Cembrit.

Specification of microsilica is shown in the appendix.

Test recipes and curing method are listed in Table 1 and table 2

Test procedure:

All of the raw materials were based on DRY weight in the recipe.

Sample preparation and measurement was according to Elkem Fibre cement lab standard. (Elkem FC lab standard, MAT-FC-20091130.801~806)

After sample production, all the samples were cured in a climate cabinet with controlled humidity and temperature for 4 days ( $23\pm 2^{\circ}\text{C}$ , 50% relative humidity) before they were subjected to the two curing regimes described below.

Afterwards, these samples were divided into 2 groups, one sample group would be exposed to  $\text{CO}_2$  regimes (modified BAC schedule); another group would continue curing in the climate cabinet at  $23\pm 2$  centigrade degree and 50% relative humidity, which was called ST condition.

BAC test (“Bescheunigte Alterung mit  $\text{CO}_2$ ”) is a method to investigate carbonation properties of fibre cement, which consists in wet/dry cycling with  $\text{CO}_2$  added in the drying stage. This method was published by Professor Benoit in the 11<sup>th</sup> IIBCC. We modified this BAC curing schedule according to the actual situation in our lab, described in table 2.

Weight variation and length variation of the sample were measured during BAC curing cycles (measured after  $\text{CO}_2$  circulation stage)

Another sample group was cured at climate at controlled situation, its variation of the weight and length was also measured as a reference.

After 124 BAC cycles, the  $\text{CO}_2$ -curing was terminated and physical properties of all the samples were investigated. The results were compared with the samples cured under standard condition.

## CONCLUSION

1. All the samples showed changes due to exposure to  $\text{CO}_2$  regimes. Carbonation had influenced several physical properties of the sheets.
2. Bending strength, moisture movement, water absorption and density were all improved mainly due to the carbonation effect; however, the bending work (toughness property) was notably decreased, and the sheets became quite brittle.
3. Shrinkage increased *only* in the samples containing 10% microsilica with 10% limestone after exposure to the  $\text{CO}_2$  environment. There was no other visible result to indicate the shrinkage increased by adding microsilica, neither when the samples were exposed to  $\text{CO}_2$  nor cured under standard condition. However the weight *increase* was reduced by when microsilica was added.
4. Thermal gravimetric analysis (TGA) shows that the amount of  $\text{CaCO}_3$  decreased with increasing dosage of microsilica, which indicates that the carbonation effect is reduced by adding MS.
5. There were no visible results in this test to show the properties of the fibre cement products were reduced due to using microsilica, or that negative carbonation effects were increased by adding microsilica.

## RESULTS AND DISCUSSION

### Physical properties

After the CO<sub>2</sub> group samples had finished 124 BAC curing cycles, all the samples were removed from the CO<sub>2</sub> regime and were soaked in the water at room temperature for two days. And the following properties were studied. Another group samples that were curing at ST condition are also studied for reference.

- WET bending strength (MOR)
- Dry density
- Moisture movement
- Water absorption
- Bending work
- Filtration time (recorded during the production)

### Bending strength (MOR)

Bending strengths are shown in figure 1.

It is indicated from figure 1 that MOR are increased after the samples have been exposed to CO<sub>2</sub> regimes for 124 cycles. Compared to the samples cured at standard condition, for the reference sample without microsilica, MOR was increased to 15.6 MPa from 13.0MPa after 124 BAC cycles.

Adding microsilica led to MOR increase, and with the dosage of Microsilica was increased, MOR was increased accordingly. MOR was increased to 15.9MPa, 16.5MPa and 16.9MPa after adding 3%, 5% and 10% microsilica respectively.

This effect of Microsilica was the same to the group of the sample curing under CO<sub>2</sub> regime or ST regime.

The addition of filler limestone does not alter the above conclusion.

### Dry density

Dry density is shown in figure 2.

Dry density was in line with the results of MOR, it was also shown that dry densities are increased after the samples were exposed to CO<sub>2</sub> regime. The addition of microsilica led to increase of density.

### Water absorption

Water absorption is shown in figure 3.

Water absorption was decreased after the samples exposed to CO<sub>2</sub> regime for 124 cycles.

All the sample curing at standard regime got 24% ~25% water absorption, and this value decreased to 16~18% for the BAC cured samples.

There were no visible differences on the water absorption of the samples which could be attributed to limestone filler or microsilica.

### Moisture movement

Moisture movement is shown in figure 4.

It is indicated from figure 4 that moisture movement is decreased after the samples have been exposed to CO<sub>2</sub> regimes for 124 cycles.

Adding microsilica tends to increase moisture movement; however, the increase in level was not visible compared with the reference samples.

The addition of filler limestone tends to reduce the moisture movement.

### **Filtration time**

Filtration time was recorded during the sheet production and shown in the figure 5.

Without the use of flocculants it is well known the filtration time increases when microsilica is used. This effect was also shown in the current test.

Without filler limestone, it can be seen from figure 5 that the filtration time was increased from 100 seconds to 400 seconds when adding 10% microsilica.

The addition of limestone filler also tended to increase the filtration time, but in a lower level.

### **Bending work**

Bending work is shown in figure 6.

Bending work could be used as an indicator to evaluate the toughness of the product. Higher bending work means higher toughness.

As indicated in fig 6, the bending work was substantially reduced after the sample had been exposed to CO<sub>2</sub> regimes, which means the toughness was decreased after exposed to CO<sub>2</sub> condition for a period. It was also shown from the bending curve that the deflection value became shorter after exposed to CO<sub>2</sub> regime for 124 cycles, which means the sample became brittle. (Figure 7)

Adding microsilica tended to increase the toughness in this test.

For the group with no filler limestone, bending work increased from the reference level 606Nmm to 890Nmm, 797Nmm and 1081Nmm when adding 3%, 5% and 10% microsilica respectively. After exposed to CO<sub>2</sub> regime for 124 cycles, the bending work of all samples were reduced significantly. However, the sample with 10% microsilica still had the highest level of 326Nmm, whereas the reference sample dropped to 177Nmm. It is indicated from the results that toughness of the samples are improved by using microsilica.

The addition of the filler limestone also tends to increase the bending work.

### **Summary**

According to the above results, we could see that physical properties of all samples were influenced when exposed to CO<sub>2</sub> regime, due to the carbonation effect.

Compared to the reference group curing at standard regime, carbonation samples had following characters after exposed to CO<sub>2</sub> regime for 124 cycles. The addition of limestone filler does not alter this conclusion.

- Increased bending strength
- Increased dry density
- Decreased moisture movement
- Decreased water absorption
- Decreased bending work, which means samples became brittle after exposed to CO<sub>2</sub> condition for a period.

The above results were attributed to the filler effect of the carbonation product CaCO<sub>3</sub>, which led to dense structure; and resulted in the higher strength, lower water absorption and lower moisture movement,

For the effect of microsilica, except the visible negative effect on the filtration time and a somewhat negative effect on the moisture movement, the other properties such as MOR, density, dry density, water absorption

and bending work were all improved by adding microsilica in this test. This applies to both curing regimes i.e. with and without carbonation.

Even it was shown from the above results that some properties were improved after carbonation, the bending work of the sample decreased significantly. This means that the toughness of the sample was decreased, and the samples became quite brittle.

Once the samples become more brittle, we believe the ability to resist the variation of humidity and temperature become weaker. As a result, cracking could occur when carbonation exceeds a critical level, especially if the product is unevenly carbonated

## Length and weight variation during exposed to CO<sub>2</sub> regime

Sample length and weight were measured periodically during curing at CO<sub>2</sub> regimes.

Shrinkage and weight variation are shown in the figure 8 to figure 15, the trend lines are also presented.

According to the results, the variation of the length and weight are following the logarithmic regulation to the BAC cycles as it was exposed to CO<sub>2</sub> regimes.

$$Y = b \ln(x) + a_0$$

Y...variation of length or weight

x...BAC cycles (CO<sub>2</sub> curing regime)

b, a<sub>0</sub>, constant

For samples exposed to CO<sub>2</sub>, the addition of microsilica leads to reduced weight *increase* due to carbonation effect, compared with the reference sample (0-sample). The addition of limestone filler does not alter this conclusion. (fig 8, fig 9)

All samples show shrinkage when exposed to CO<sub>2</sub>. (fig 10, fig 11)

1) For samples with no limestone, there is a tendency that the shrinkage is increased as microsilica is added; but the increased level is not visible compared to the reference sample without MS. (Fig 10). Therefore the shrinkage is at the same level regardless if 3%, 5% or 10% microsilica is used. Reference sample showed 0.11% shrinkage and other samples with microsilica showed around 0.16%.

2) The addition of limestone filler may seem in itself (i.e. without microsilica) to lead to increased shrinkage. With no filler limestone, shrinkage of the reference sample without MS is 0.11 % (fig 10); with 10% limestone it becomes 0.15% (fig 11).

3) For the samples containing 10% limestone filler, the addition of up to 5% microsilica does not seem to affect the shrinkage in a significant way. However, the sample containing 10% filler and 10% microsilica shows a marked increase in shrinkage (fig 11), it increased to 0.25% after 124 cycles.

For "standard" curing regime (i.e. samples not exposed to high CO<sub>2</sub>), shrinkage tends to decrease with increasing dosage of microsilica (fig 12); weight increase was also reduced (fig 14). This applies to samples without filler limestone; samples with 10% limestone show no significant influence of microsilica (fig 13 & fig 15).

## Cement hydrated phases and CO<sub>2</sub> content

Cement hydrated phase of the sample was investigated by XRD and TG/DSC analysis.

### XRD analysis

XRD pattern of the samples curing under standard situation are shown in figure16 and figure17; XRD pattern of the sample exposed to CO<sub>2</sub> (BAC test) are shown in figure 18 and figure 19.

It is indicated from figure 16 and figure 17 that the phase  $\text{Ca(OH)}_2$  is reduced with increased microsilica dosage. This is probably due to the pozzolanic effect of microsilica. It is further found that no  $\text{Ca(OH)}_2$  is detected after the samples have been exposed to  $\text{CO}_2$  (BAC) (figure 18 and figure 19). This is probably due to the carbonation effect.

### Thermal gravity analysis (TG)

For cement hydrated product, the phase amount in the composite could be quantified by thermal gravity analysis (TG).  $\text{CaCO}_3$  would be decomposed at  $\sim 800$  degrees centigrade, which results in a measurable heating absorption phenomenon, and mass loss from released  $\text{CO}_2$ , and this  $\text{CO}_2$  amount is in line with the amount of  $\text{CaCO}_3$ , which can be used as an indicator to evaluate the carbonation effect. This thermal character of  $\text{CaCO}_3$  can be shown in a TG/DSC curve. A typical TG/DSC curve of cement hydrated product is shown in figure 20.

TG analysis results are shown in figures 21 to 24. The  $\text{CO}_2$  amount results are shown in the figure 25.

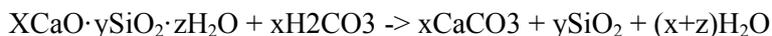
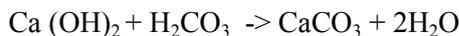
For the group *without* filler limestone curing at standard condition,  $\text{CO}_2$  amount was 7.1%, 4.6%, 2.4% and 2.3% when the dosage of microsilica was 0%, 3%, 5% and 10% respectively. This indicates that  $\text{CaCO}_3$  is decreased when the dosage of microsilica is increased. For the carbonation sample, even though the amount  $\text{CaCO}_3$  because of carbonation was high compared to the reference samples cured at standard situation, this conclusion was not changed.  $\text{CO}_2$  was decreased to 5.4% from 8.2% when the dosage of microsilica was increased to 10%.

The addition of filler limestone does not alter the above conclusion. For the group cured at standard situation,  $\text{CO}_2$  amount decreased to 5.8% from 10.4%; For the carbonation sample,  $\text{CO}_2$  decreased to 7.8% from 13.5% when the dosage of microsilica was increased to 10%.

According to TG and XRD analysis, it is demonstrated that the carbonation effect of the sample is reduced by adding microsilica.

## DISCUSSION

Carbonation has been described a reaction between hydrated product ( $\text{Ca(OH)}_2$ , C-S-H) created by cement hydration, and  $\text{CO}_2$  exposure from outside. It is an inherent reaction to cement-based products, taking place also in fibre cement products under the 'right' conditions. The reaction between the  $\text{Ca(OH)}_2$  and  $\text{CO}_2$  is the dominating part among these reactions



Weight of the sample would be increased as the carbonation implies that  $\text{CO}_2$  from the outside is absorbed into the system.

On the other hand, sample weight is also influenced by the hydration process. Cement product is a matrix with complex pore structure filled with pore water of high pH. All of the elements/species inclusive  $\text{CO}_2$  are influencing such a pore system. Moisture is also an important factor. As the environment humidity is changed, it could influence the weight of the sample too as the moisture is lost or absorbed.

Carbonation is influenced by several factors, such as the content of  $\text{Ca(OH)}_2$ , pH- level, diffusion index of  $\text{CO}_2$  in the matrix and so on.

Especially the diffusion index of  $\text{CO}_2$  will give visible influence on the carbonation. The diffusion index is strongly depending on the pore structure of the matrix. The diffusion index of  $\text{CO}_2$  will be decreased as the structure become finer and denser. Under such a condition carbonation reaction would be slowed down and become less complete. Moreover, some of the  $\text{CaCO}_3$  created by the carbonation may also act as a fine filler and make the matrix denser, in itself leading to retardation and reduced carbonation.

However, a denser structure may also lead to higher stress when the moisture moves into the pore structure due to capillary effect. Carbonation may also result in higher stress due to increase of the solid phase volume was compared to its initial status. Both of these reactions might result in delayed shrinkage, even cracking when exceeding a critical level.

For the effect of microsilica, we know microsilica will react with  $\text{Ca}(\text{OH})_2$  and create more binder in the fibre cement product, which gives higher strength and a more dense structure. Carbonation would be reduced due to the less  $\text{Ca}(\text{OH})_2$  and denser structure. So the weight created by carbonation could be reduced accordingly. However, denser structure may also make higher stress as the moisture is moving in the product (due to capillary effect). So the shrinkage could be increased when the matrix is not strong enough to resist the stress created by carbonation and moisture movement. Cracking may occur as this shrinkage exceeds a critical level, more cracks may result in more  $\text{CO}_2$  entering into the product, thus enhancing the problem.

So we believe the effect of microsilica on the shrinkage of fibre cement product may have both advantages and disadvantages. The advantage is to consume  $\text{Ca}(\text{OH})_2$  and increase the structure density, thus both reducing the amount of  $\text{CO}_2$  that enters into the matrix, and reduce the amount of  $\text{Ca}(\text{OH})_2$  available for carbonation. The disadvantage may be a higher stress as the moisture moves along the finer pore structure, due to capillary effect (drying shrinkage). According to the Kelvin – Laplace theory, liquid surface tension in the capillary would be mainly related to the diameter of the capillary, i.e. lower diameter means higher liquid surface tension. Moisture movement is always happening in cement-based materials due to unbalanced humidity level. For the material with complex pore structure, like fibre cement, liquid surface tension in these pores would be created as the moisture is moving along these channels due to capillary effect, and this tension create stress to the structure and make the shrinkage, i.e. drying shrinkage; The effect of the latter could be cracking, if it exceeds a critical level.

## REFERENCES

- [1] Benoit de Lhoneux, selected issues of fibre-cement sustainability: wood Pulp refining energy and accelerated ageing of Fibres and composites, 11th IIBCC 2008, Madrid.
- [2] Benoit de Lhoneux, the microstructure and ageing of cellulose fibre reinforced autoclaved fibre cement composites. International Journal of Cement Composites and Lightweight Concrete, Volume 11, Issue 2, May 1989.
- [3] H.Savastano, Comparisons of different synthetic fibres as the main reinforcement of air cured fibre cement , 10th IIBCC 2006, Sao Paulo
- [5] Internal report, Elkem Fibre cement lab.

**Table 1 Tested recipes and curing method**

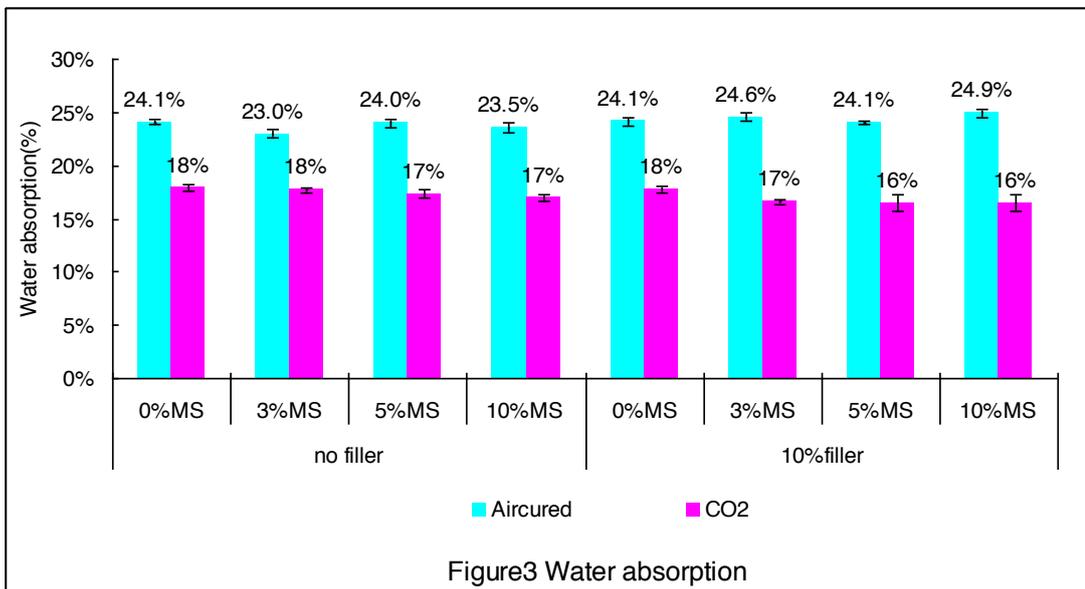
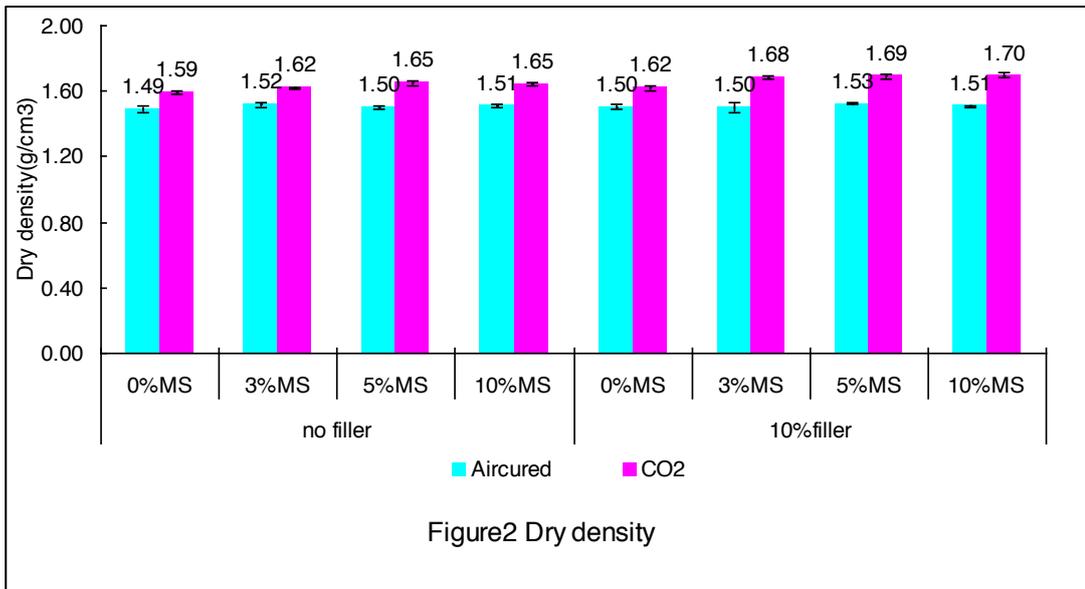
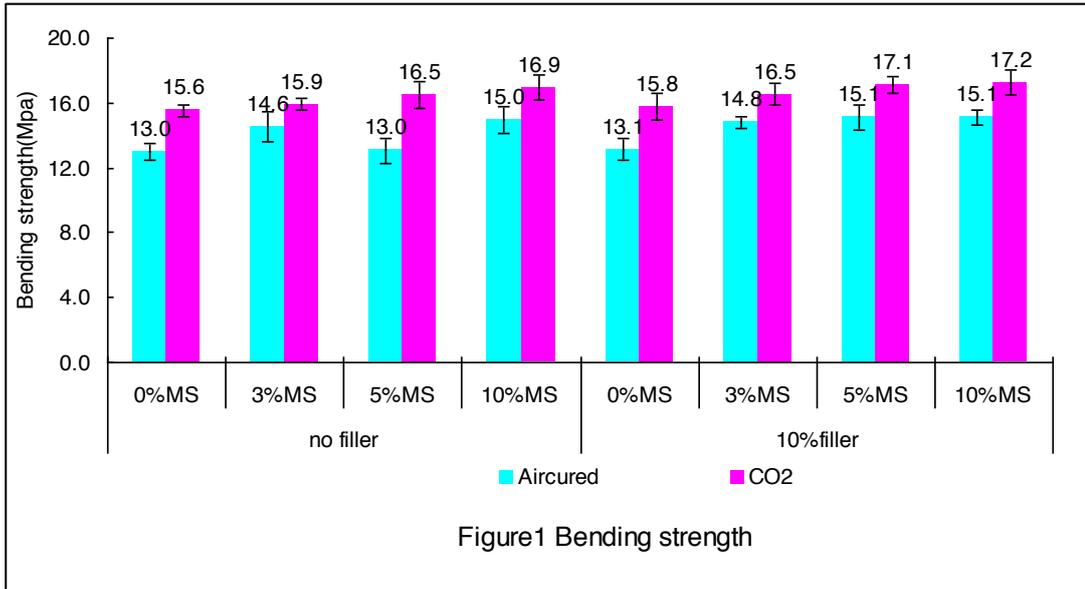
Sample ID	P.O cement	PVA	Pulp	Microsilica	Limestone	Curing method
CB 1	94.5%	2.0%	3.5%	0.0%	0.0%	ST*
CB 2	91.5%	2.0%	3.5%	3.0%	0.0%	ST
CB 3	89.5%	2.0%	3.5%	5.0%	0.0%	ST
CB 4	84.5%	2.0%	3.5%	10.0%	0.0%	ST
CB 5	94.5%	2.0%	3.5%	0.0%	0.0%	CO <sub>2</sub>
CB 6	91.5%	2.0%	3.5%	3.0%	0.0%	CO <sub>2</sub>
CB 7	89.5%	2.0%	3.5%	5.0%	0.0%	CO <sub>2</sub>
CB 8	84.5%	2.0%	3.5%	10.0%	0.0%	CO <sub>2</sub>
CB 9	84.5%	2.0%	3.5%	0.0%	10.0%	ST
CB 10	81.5%	2.0%	3.5%	3.0%	10.0%	ST
CB 11	79.5%	2.0%	3.5%	5.0%	10.0%	ST
CB 12	74.5%	2.0%	3.5%	10.0%	10.0%	ST
CB13	84.5%	2.0%	3.5%	0.0%	10.0%	CO <sub>2</sub>
CB14	81.5%	2.0%	3.5%	3.0%	10.0%	CO <sub>2</sub>
CB15	79.5%	2.0%	3.5%	5.0%	10.0%	CO <sub>2</sub>
CB16	74.5%	2.0%	3.5%	10.0%	10.0%	CO <sub>2</sub>

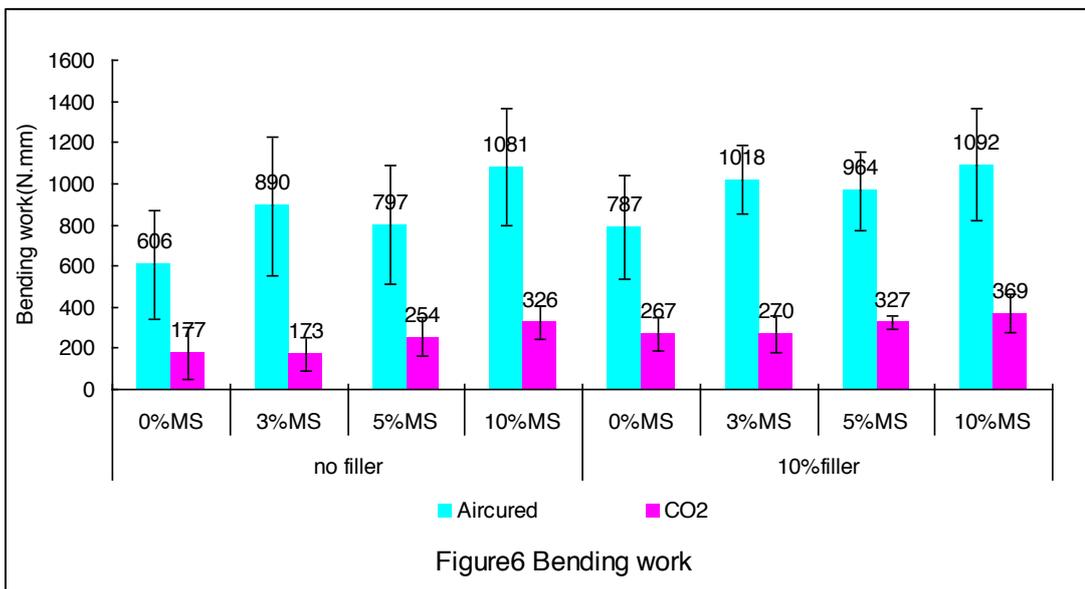
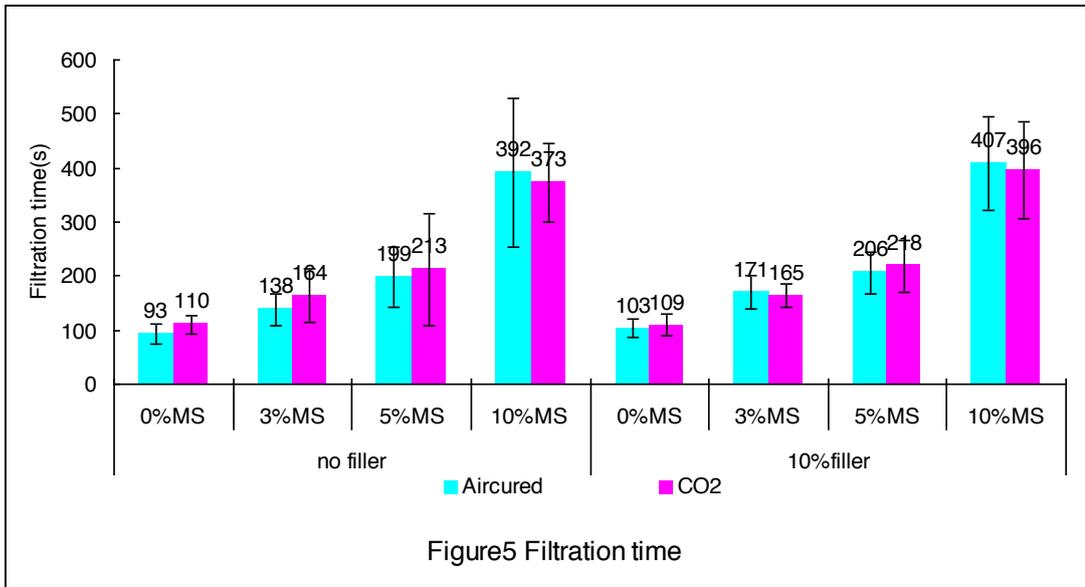
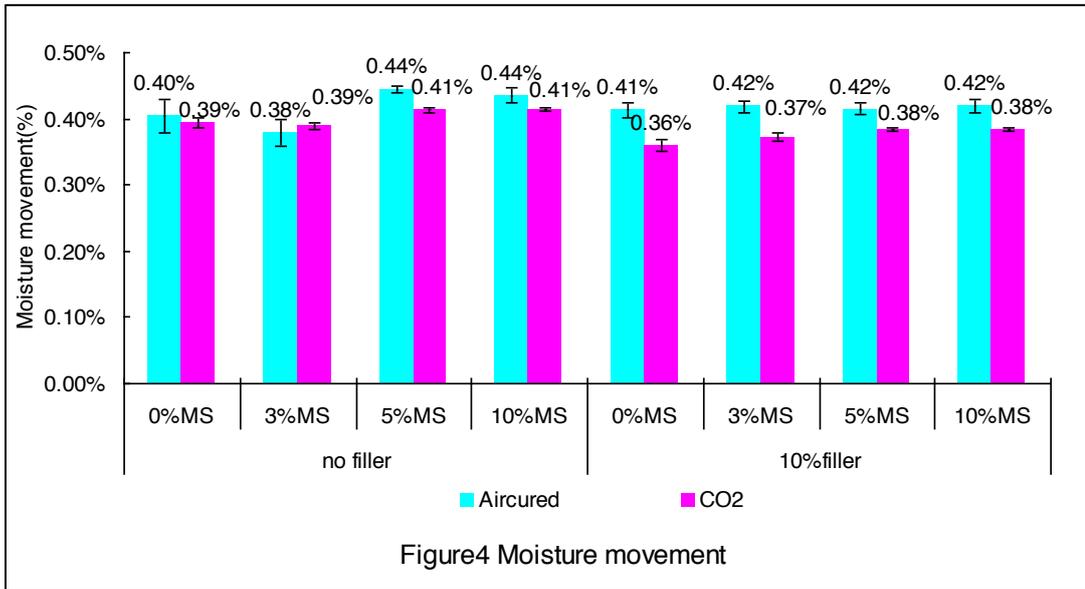
ST: Standard curing schedule, 23±2C, 50RH

CO<sub>2</sub>: Modified BAC curing schedule, table 2.

**Table 2 Modified BAC curing schedule**

Modified BAC curing schedule	Time
Submerged in water, ambient temp	12 hours
Drying at 65 degree	1 hours
Cooling, ambient temp	1 hours
CO <sub>2</sub> circulation, 60RH,30 degree	5 hours
Drying at 65 degree	5 hours
Recycle...	-
Total hours per cycle	24 hours





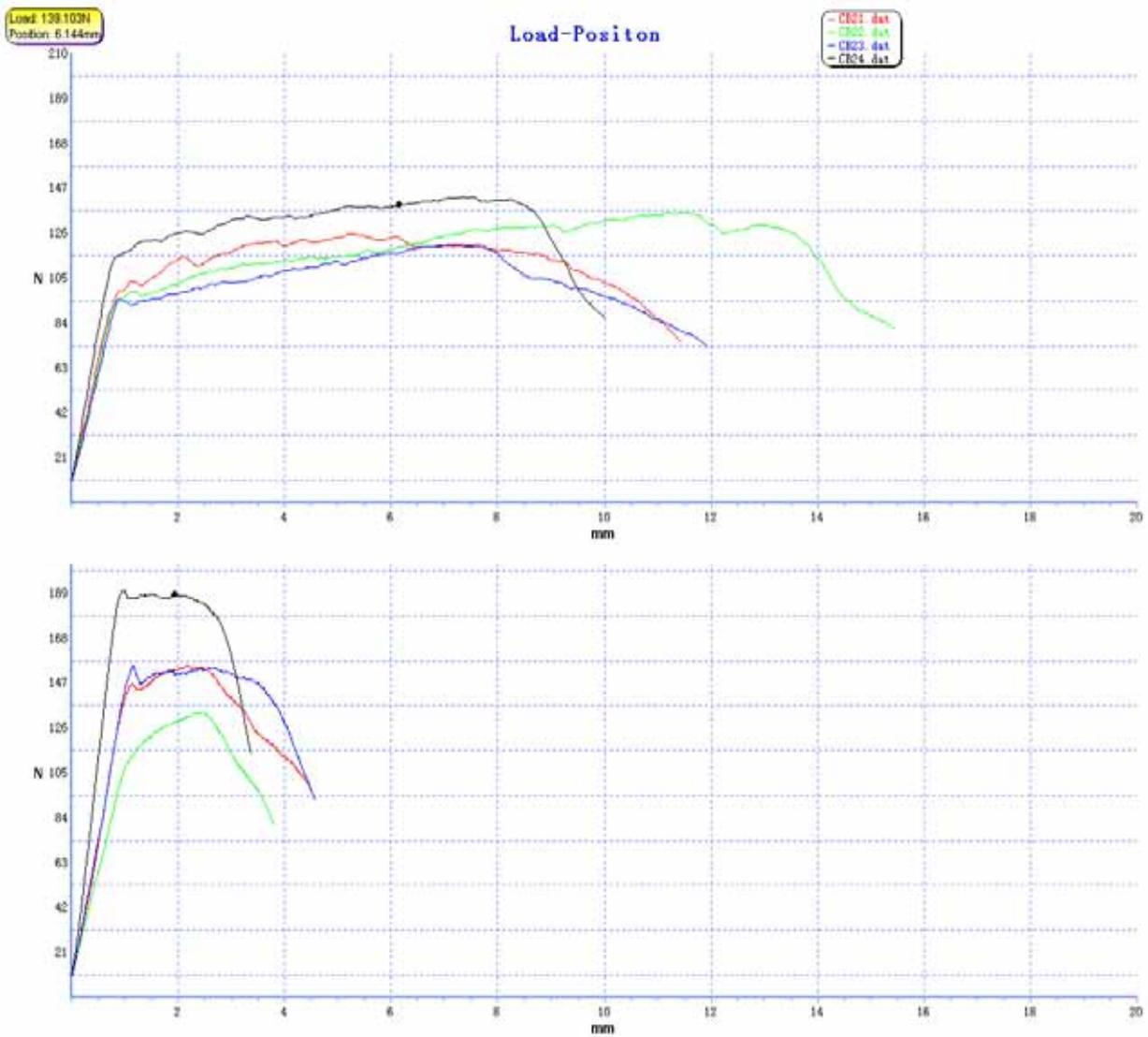


Figure 7 Bending curve-3% MS sample, no limestone

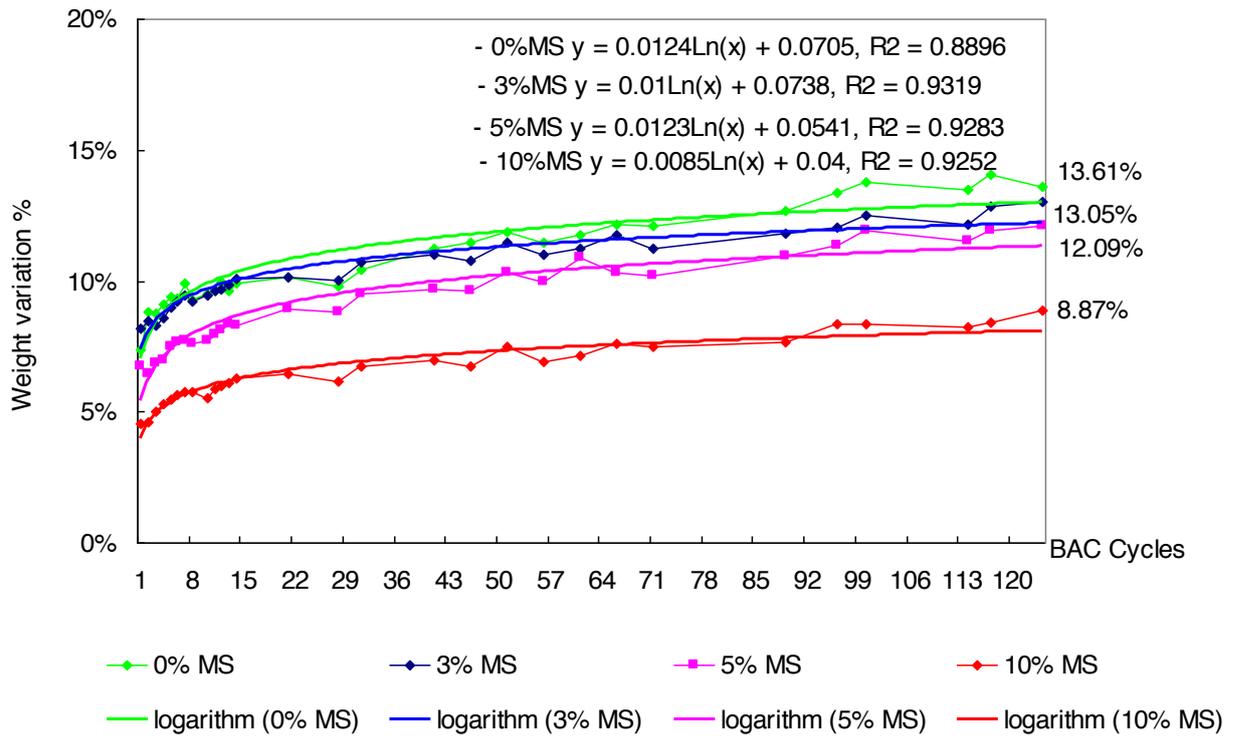


Figure8 Weight variation with modified BAC curing schedule

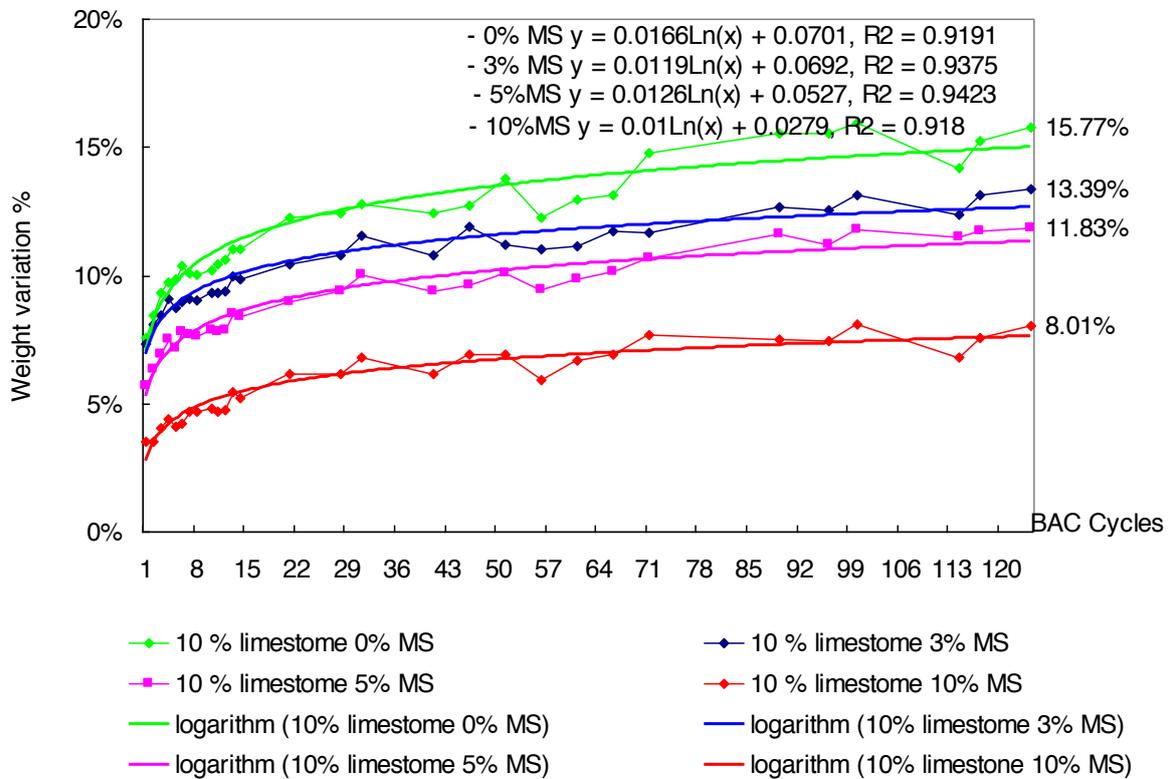


Figure9 Weight variation with modified BAC curing schedule, 10% limestone

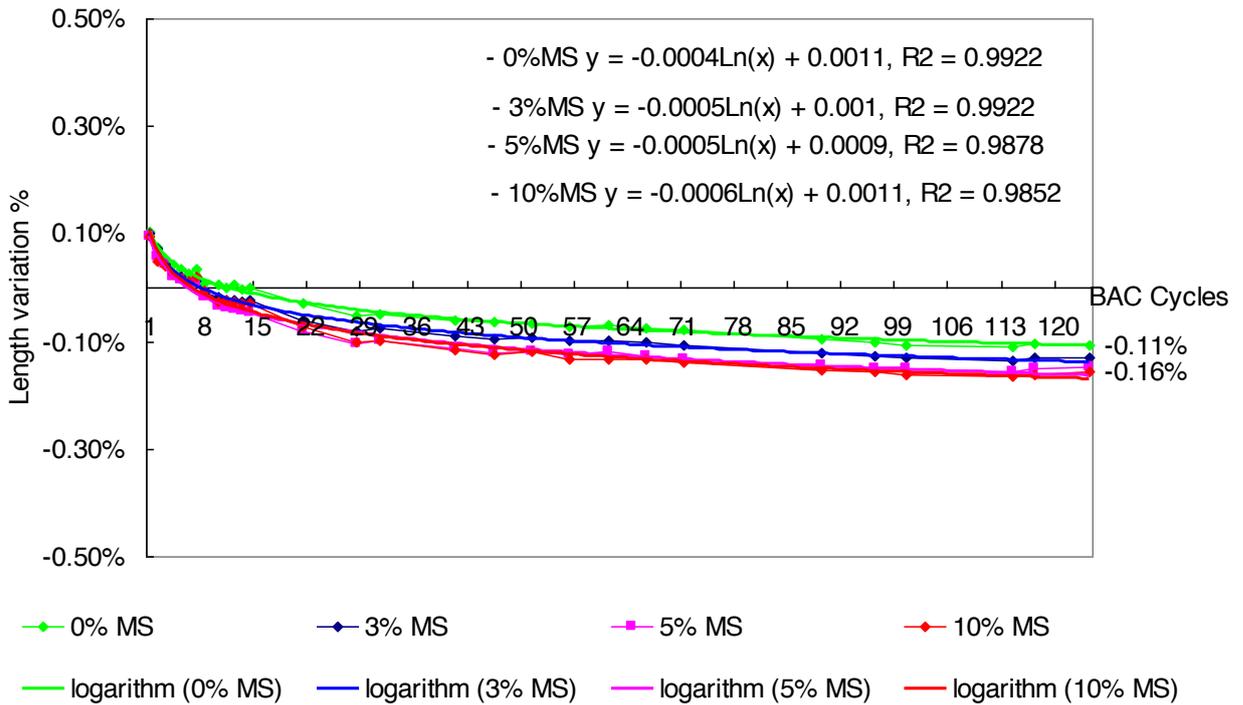


Figure10 Length variation with modified BAC curing

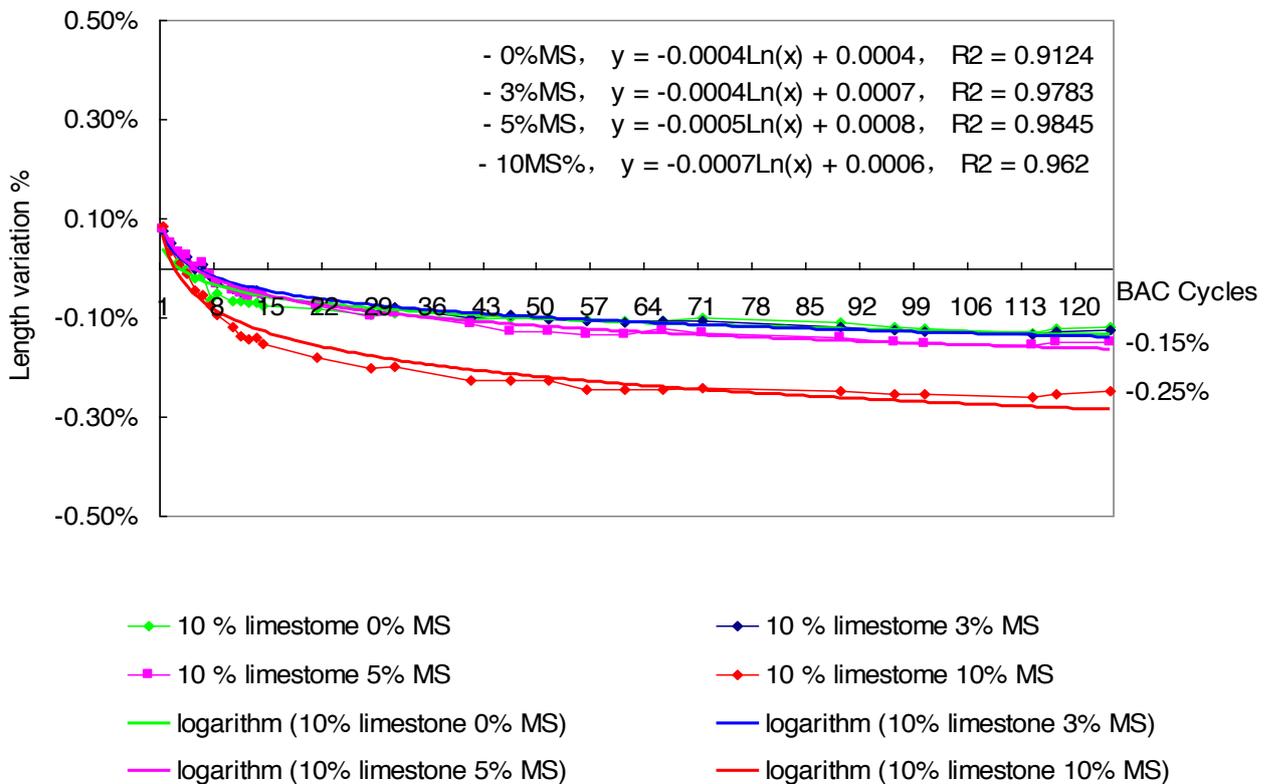


Figure11 Length variation with modified BAC curing, 10% limestone

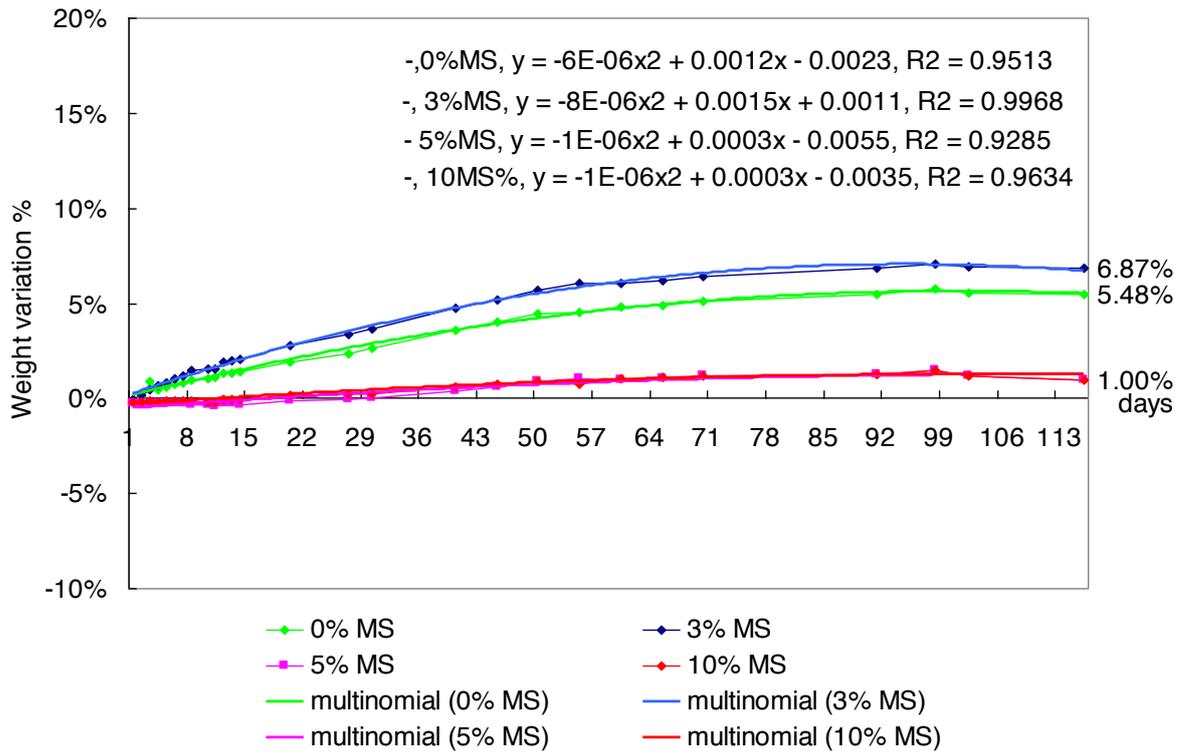


Figure14 Weight variation with ST curing

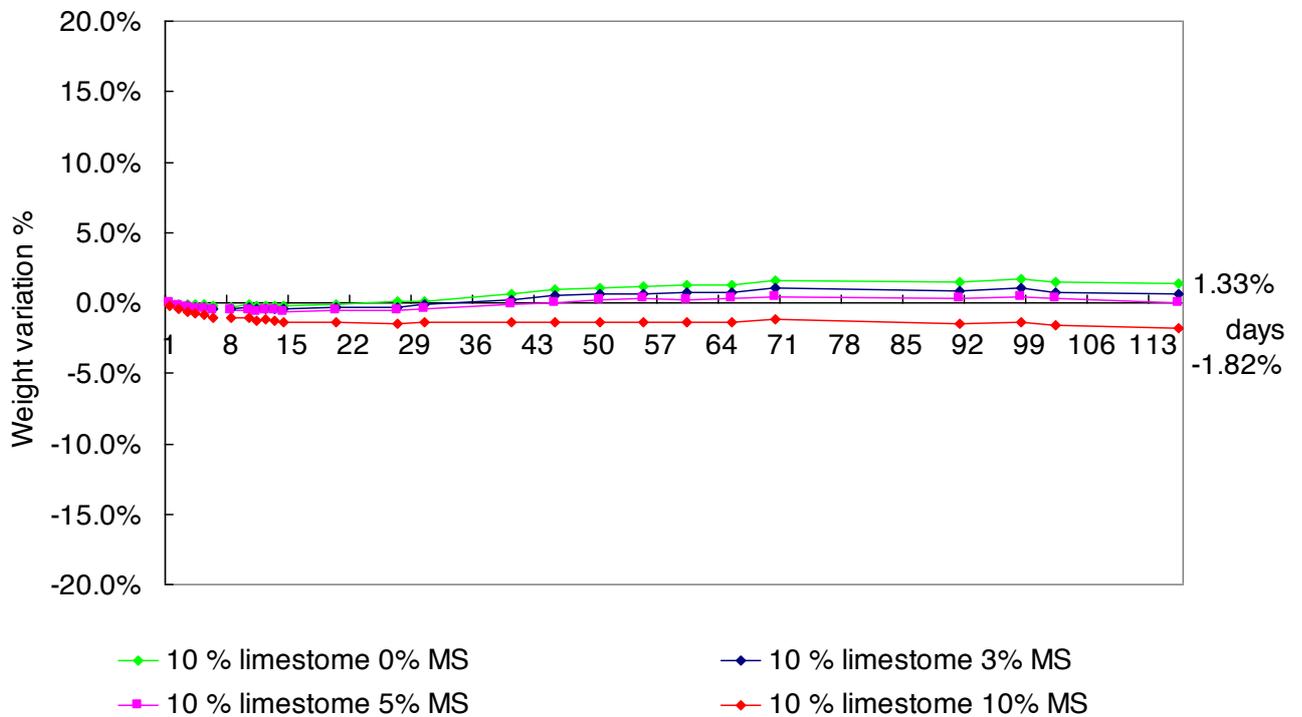


Figure15 Weight variation with ST curing, 10% limestone

O : Ca(OH)<sub>2</sub> ;      X : CaCO<sub>3</sub>      + : β -Ca<sub>2</sub>(SiO<sub>4</sub>)

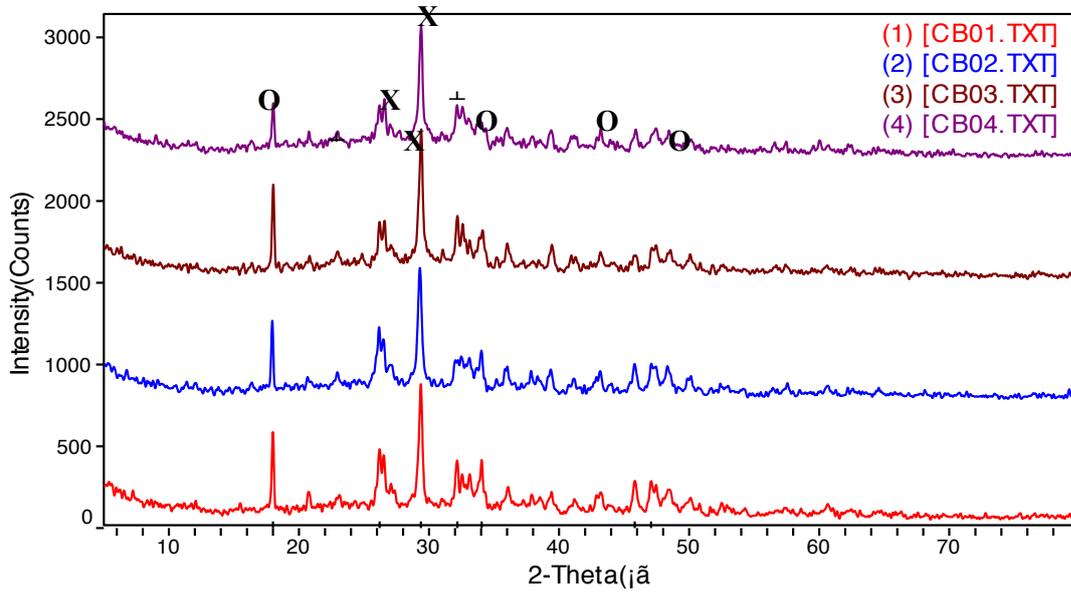


Figure 16 XRD pattern of the samples curing under standard situation

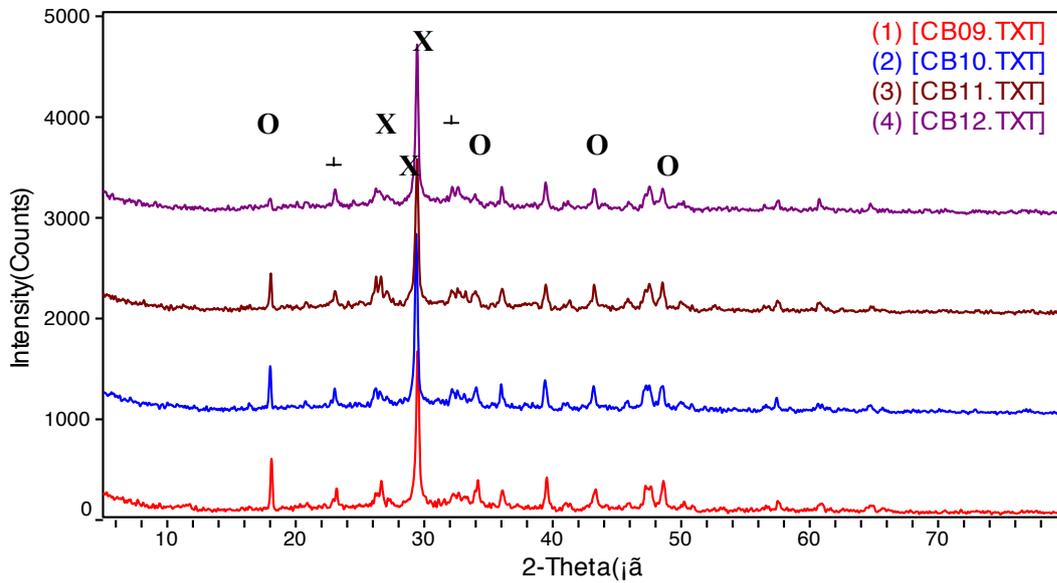


Figure 17 XRD pattern of the samples with 10% filler limestone

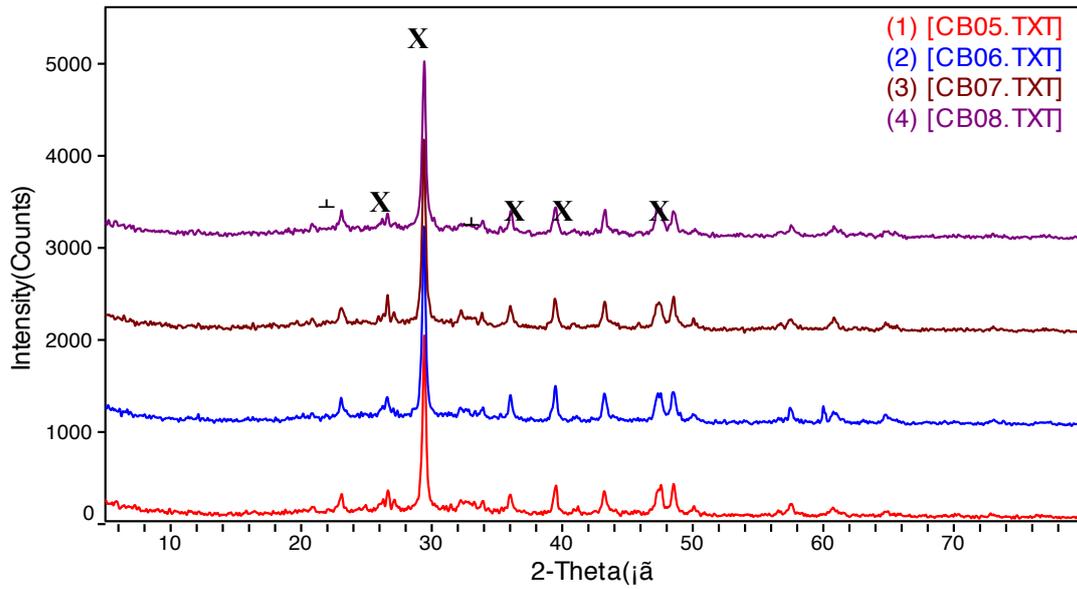


Figure 18 XRD pattern of the samples exposure to CO<sub>2</sub> (BAC) regimes

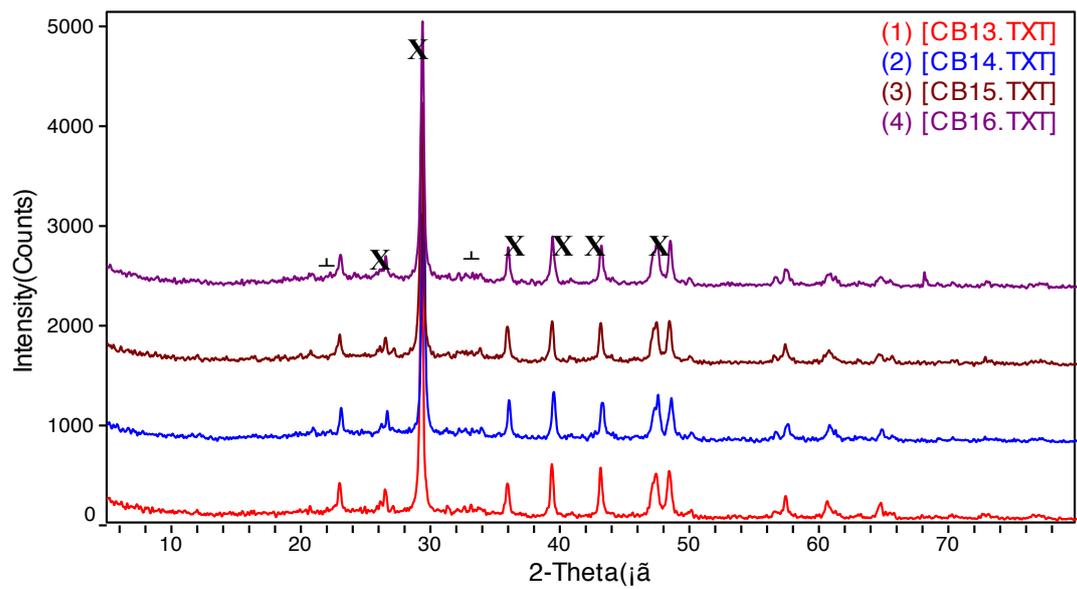


Figure 19 XRD pattern of the samples with 10% filler limestone exposed to CO<sub>2</sub> (BAC) regimes

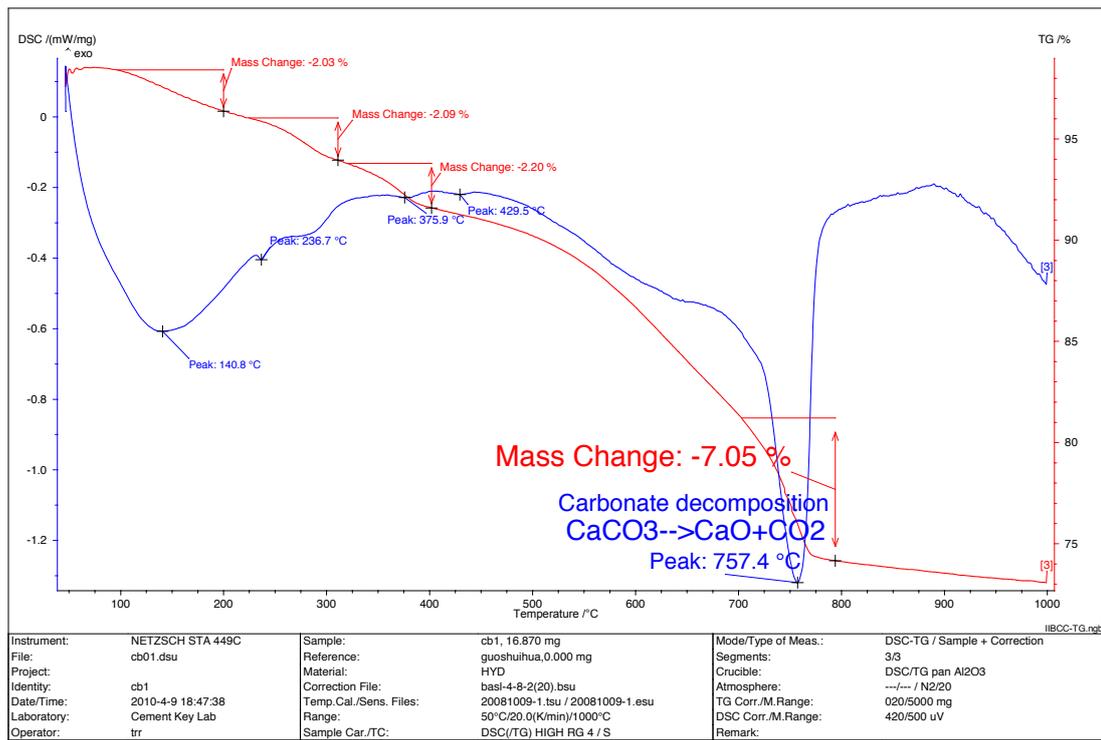


Figure 20 TG/DSC curve of P.O I cement hydrated product (eg, CB1)

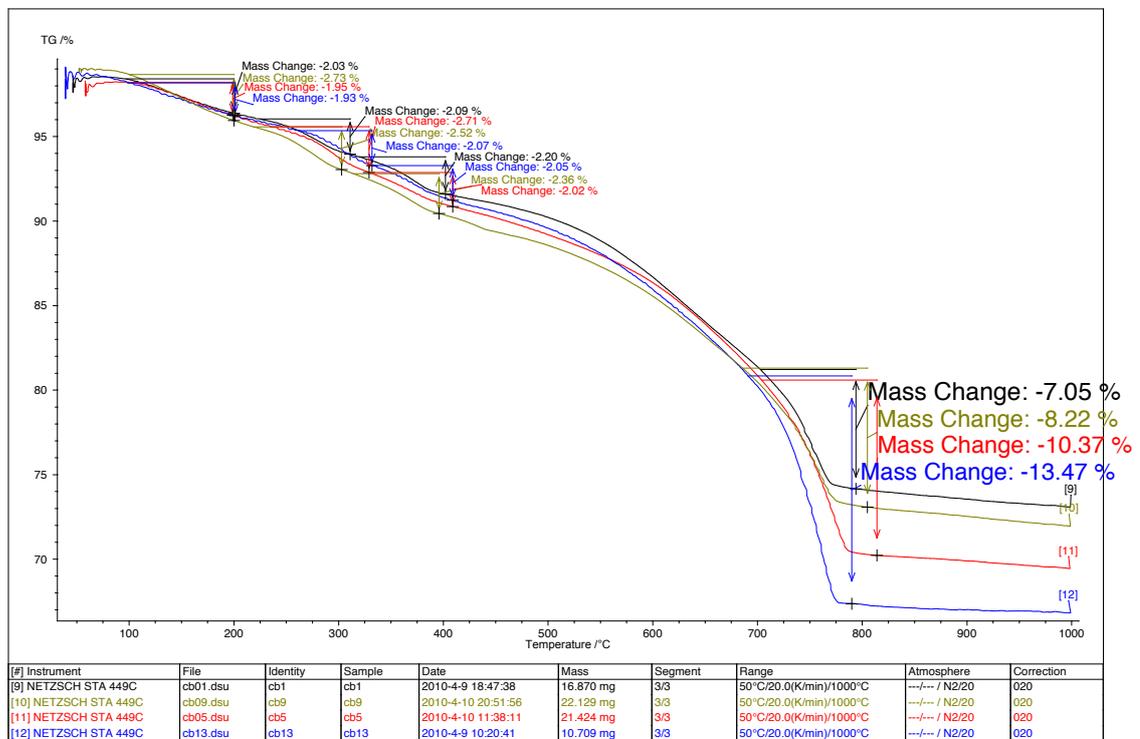


Figure 21 TG curve of the reference sample without microsilia.

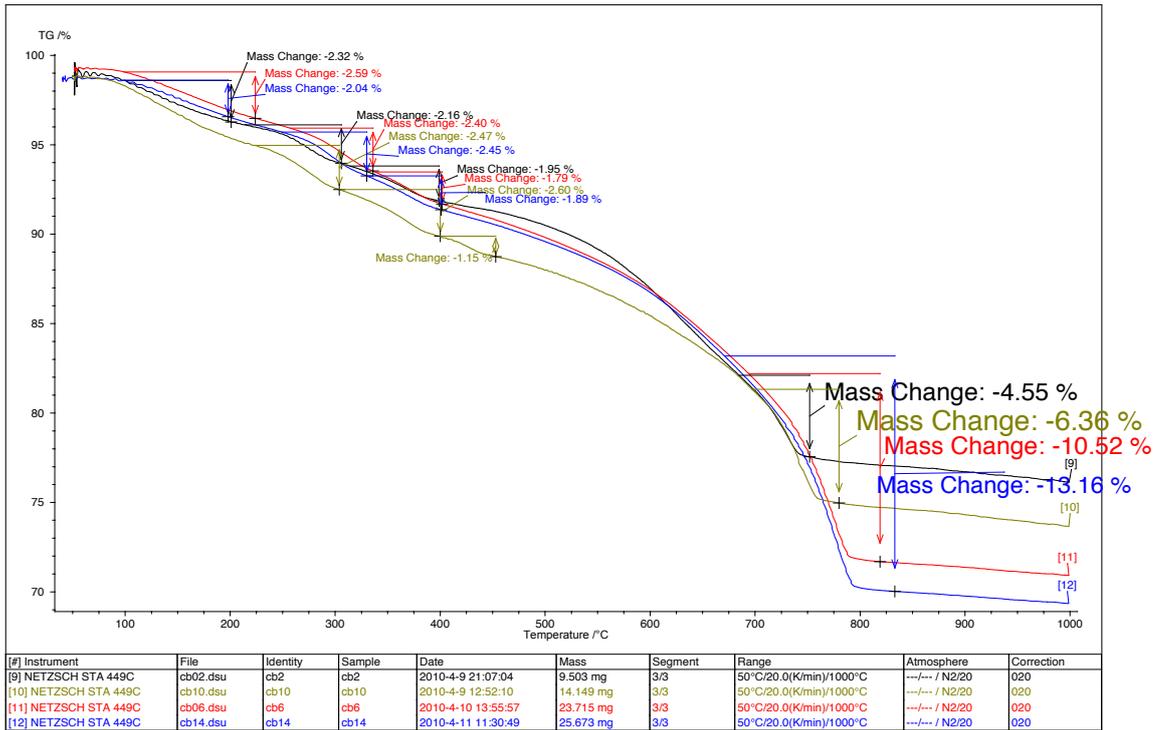


Figure 22 TG curve of the reference sample with 3% microsilica.

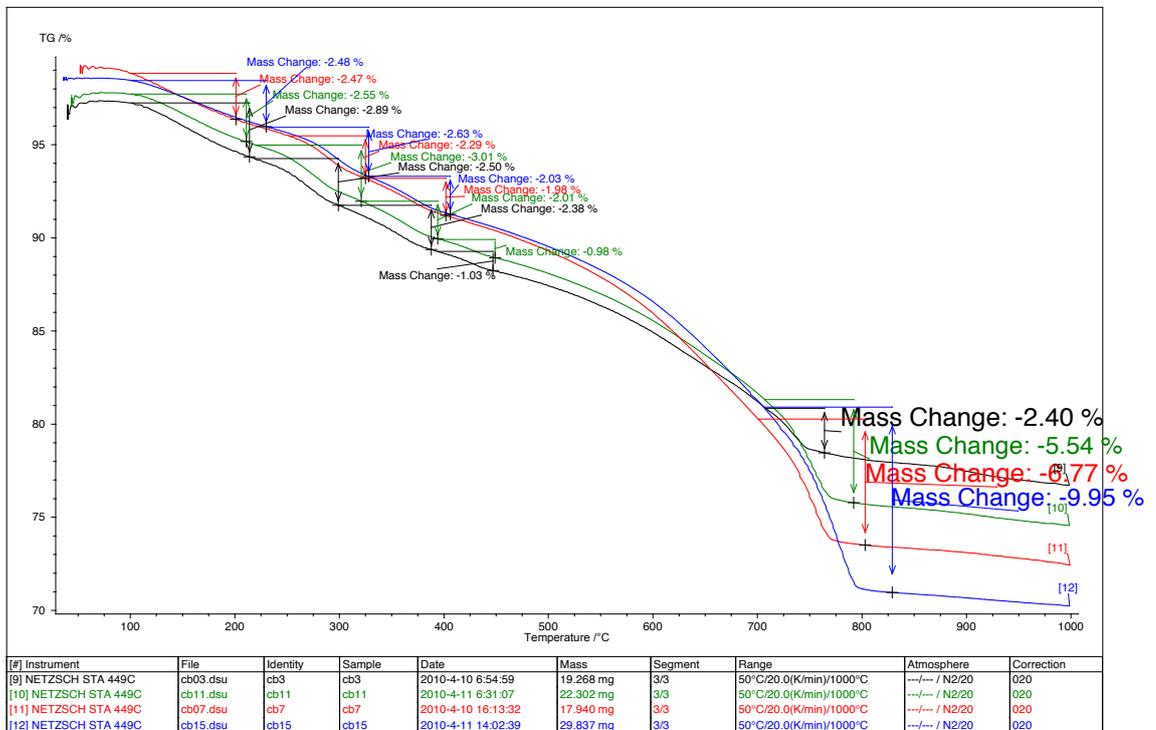


Figure 23 TG curve of the reference sample with 5% microsilica.

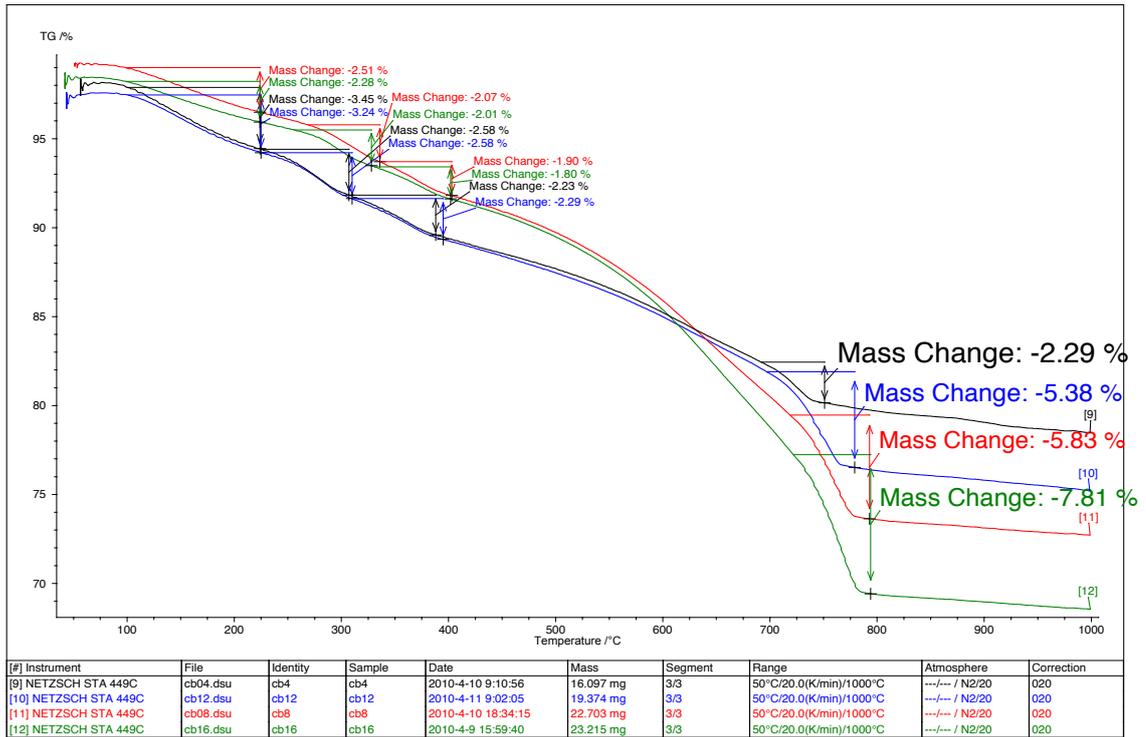


Figure 24 TG curve of the reference sample with 10% microsilia.

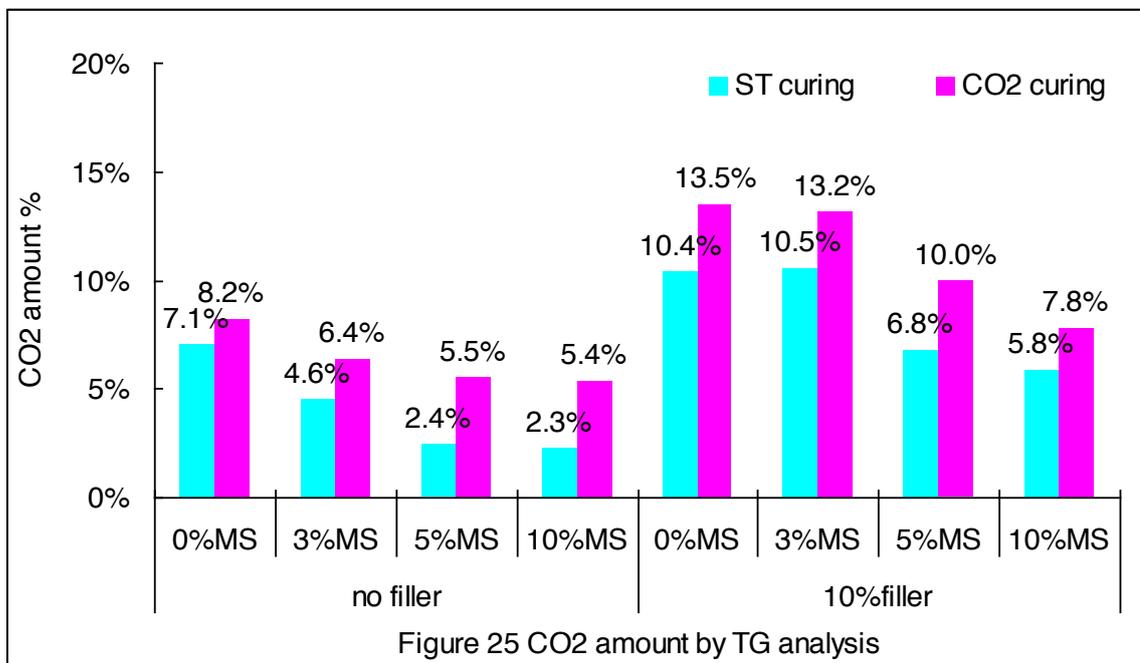


Figure 25 CO2 amount by TG analysis

**APPENDIX**

## Microsilica (HG)

%	SiO <sub>2</sub>	94.24
%	H <sub>2</sub> O	1.10
%	LOI950	2.48
Kg/dm <sup>3</sup>	Bulk density	0.22
%	+0.045mm	0.80
%	C	1.92
%	SiC	0.27
-	pH	7.2
%	Fe <sub>2</sub> O <sub>3</sub>	0.02
%	Al <sub>2</sub> O <sub>3</sub>	0.11
%	CaO	0.28
%	MgO	0.80
%	Na <sub>2</sub> O	0.08
%	K <sub>2</sub> O	1.72
%	P <sub>2</sub> O <sub>5</sub>	>0.23
%	SO <sub>3</sub>	0.62
%	Cl	0.004