# *EFFECT OF SILICA DISSOLUTION ON THE MECHANICAL PROPERTIES OF ALKALI REACTIVE BASALT

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**Abstract**

This paper focuses on the microstructural deterioration of reactive basalt under the attack of aggressive NaOH solution. Small rock samples were prepared and cured in 1M NaOH and 4M NaOH solutions at 80°C for 3 weeks and 4 days, respectively. The aim of the study was to characterize stress-deformation performance of attacked and pristine basalt samples. Mechanical experiments were carried out by means of controlled micro-tensile equipment in which very small rock or concrete specimens can be tested. Additionally, the microstructure of the specimens was characterized by electron microscope. It was found that aggressive alkaline environment dissolves glass phase significantly and reduces the mechanical quality of alkali reactive basalt aggregate considerably. Fully dissolved basalt has roughly 4 times lower tensile strength and elastic modulus in comparison with pristine basalt.

**Keywords**: alkali-silica reaction, silica dissolution, microstructure, micromechanics, basalt

## 1 INTRODUCTION

Dissolution of reactive siliceous components of aggregate in highly alkaline cement paste pore solution triggers alkali silica gel formation. Upon formation, the gel can imbibe water, swell and render distress in the cement matrix. In case the generated stress exceeds tensile strength of paste, cracks develop and propagate in the system.

The mechanism of silica dissolution is not so much controlled by the alkali species Na and K, but rather by water molecules and dissolved OH-ions breaking silica bonds, which then later recombine with alkali [1-3]. Garcia-Diaz et al [4] showed that the siloxane bond breaking up to form Q3 tetrahedrons prevails over the dissolution during the swelling step. The formation of Q3 tetrahedrons causes a swelling of the aggregate and a significant increase of its specific pore volume due to micro-cracking. Leeman and Holzer [5] studied the dissolution of silica and other minerals in various igneous, sedimentary and metamorphic aggregate in 2M NaOH solution at 38 °C during two weeks. They observed that mica and feldspar crystals in the aggregates dissolved less frequently than quartz while feldspars dissolve more than mica. It was reported that mica and feldspar phases are a common source for alkali ions and may influence the pore solution chemistry in cement paste and affect ASR gel formation [6].

However, cement paste is not the only component which is deteriorated upon silica dissolution and gel formation. The authors' earlier studies showed that reactive aggregates such as west Anatolian basalt can become highly porous after dissolution of glass component in its ground mass after 1M NaOH attack at 80°C [7]. This should bring alteration of micromechanical properties of the aggregate which is a significant parameter in ASR damage and its consequences regarding structural stability.

In this paper, authors do not focus on the silica dissolution kinetics or rate but rather focus on its consequences on the integrity of the concrete and the importance of the micromechanical properties of silica-dissolved zone of an alkali reactive aggregate. The aim was to characterize the effect of high pH on the micromorphology of the alkali-reactive basalt. Furthermore, the realistic micromechanical properties of the pristine and the etched aggregate were determined to be used in a future computational model study.

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## 2 MATERIALS AND METHODS

### 2.1 Materials

The aggregate used in this study is an alkali reactive clinopyroxene-olivine basalt, which contains ~45% matrix with a composition of 3/4 basaltic glass and ¼ plagioclase. The aggregate showed 0.833% accelerated mortar bar test expansion at 14 days (*cf* ASTM C1260 [8]). Details on the characterization of the aggregate can be found elsewhere [7].

### 2.2 Curing

The test specimens were extracted from a basalt core. Rock pieces were cut into 15×15×15mm$^3$ cubes and a nodge was created in the specimens as shown in Figure 1. The idea was to dissolve glass phase out of the basalt specimens and determine the micro-mechanical properties of the affected aggregate. For this aim, two series of specimens were cured in different aggressive solutions. First series was cured in 1M NaOH solution at 80°C for 3 weeks and the second one in an extremely aggressive 4M NaOH solution for 4 days in order to ultra-accelerate the dissolution of the glass phase. In addition to the exposed specimens, a group of pristine (control) specimens were also saved for the tensile strength testing. At the end of the curing period the specimens were washed with tap water. Specimen identification is summarized in Table 1.

### 2.3 Electron microscopy

Broken specimens were investigated using a *Philips XL30* environmental scanning electron microscope (ESEM). The instrument was operated at 20kV accelerating voltage, beam current 20mA, 0.5Torr pressure and at 10 mm working distance, with these settings applied for imaging analysis. Analysis was carried out on the qualitative basis. Detection was done by the backscattered electron (BSE) detector.

### 2.4 Micro-tensile test

A *Kammrath & Weiss* 5000 N tensile/compressive module was used for the micro-tensile test. The load was applied symmetrically; therefore the ends of the specimens were displaced equal distances away from the area of interest. The displacements were measured by micro-gauge mounted on the specimens. This displacement was used as feedback signal for the closed loop system. The rate at which the displacement is applied was 0.0136 μm/s.

### 2.5 Image analysis

Determination of required dimensions *i.e.* broken cross-section area, thickness and eccentricity is carried out by *ImageJ*, a freeware image analysis software [9]. Furthermore, leached out and pristine areas of the basalt specimens were segmented by threshold filter and measured by the software. Dissolved zone can be easily distinguished by its light colour compared to the typical dark appearance of pristine basalt (Figure 2).

## 3 RESULTS

### 3.1 Microstructure study

As it can be realized by the ESEM study that basalt microstructure is dense (Figure 3). In principle, its dense matrix with volcanic glass and lath-like plagioclase crystals among the phenochrysts is quite advantageous from strength and permeability points of view. However, amorphous or cryptocrystalline silica is known to be very soluble at high pH. The electron microscopy study in this project also showed that the microporosity of alkali-reactive basalt was significantly coarsened by the high pH NaOH solutions. In Figure 4 (a, b), etched-out basalt matrix due to the glass dissolution can be seen clearly. The most significant finding was the etched-out basalt matrix containing stacked plagioclase crystals between the olivine and pyroxene phenocrysts. It should be noted that according to the ESEM observations, after 3 weeks, 1M NaOH solution leached the glass component out but did not affect plagioclase minerals visually (Figure 5a). Evidence was spotted at the transition zone between dissolved area and pristine matrix that the glass dissolution does not continue from the rim into the body but it rather dissolves in a way that it leaves a network of volcanic glass (Figure 5a). However, it was observed that extremely aggressive 4M NaOH started to dissolve the grain boundary (i.e. [101] or [100]) of the plagioclase crystals and increased their porosity (Figure 5b).

### 3.2 Micro-mechanical testing

The effect of glass dissolution on the micro-mechanical properties of the basalt is summarized in Figure 6, 7 and Table 2. The graphs express the flexural stress versus the crack opening measured by the micro-tensile apparatus. The test has monitored the force generated per deformation increments so the flexural stress is calculated according to the following formula:

$$\sigma = \frac{F}{b \cdot h} + \frac{6F \cdot e}{b \cdot h^2} \quad (1)$$

Where $F$ is the maximum force determined, $b$ is the width of the broken cross section, $h$ is the height of the cross section and $e$ is the eccentricity of the center of the cross-section (see also Figure 1).

In Figure 6, complete cross-section is taken into account. In the BAS_P series specimens, the cross-sections contained non-dissolved matrix while in the BAS_4M specimens they were completely dissolved. However, the BAS_1M series had partial dissolution therefore when the complete cross-section was used in the stress calculation; they naturally exhibited lower strength, which is purely because of the dissolved zone.

In order to have an idea about the micromechanical properties of the dissolved zone, this zone is isolated from the pristine zone and stresses are recalculated accordingly. The recalculated results are presented in Figure 7 and Table 2. Two distinct flexural strength zones can be noticed clearly, 30-40MPa zone and 3-9 MPa zone.

In Figure 7 only the pristine part of the cross section is taken into account. It should be noted that the completely dissolved aggregate (1 Molar and 4 Molar) have a lower strength and also a lower E-modulus. In order to relate the tensile strength to the flexural strength, the flexural strength has to be divided by a factor between 2 and 3. Neville [10] gives a factor of 2 and the Eurocode [11] takes the size of the specimen into account. For the size used in these tests the factor is suggested as 2.9.

Pristine specimens revealed consistent results in the micro-tensile testing. Considering the flexural tensile strength of complete cross-section of pristine basalts, the strength values are found to be approximately 34 MPa. Partial dissolution of basalt after curing in 1M NaOH for 3 weeks reduces the flexural strength of complete cross-section to 15-20 MPa. Fully dissolved specimens exhibited flexural strength values between 3-9 MPa. Recalculated (only pristine part is considered) flexural strength values show that pristine and partly dissolved basalt samples has flexural strength values between 30-40 MPa and flexural strength of fully dissolved basalt is 3-9 MPa. The findings are found to be in line with the literature (*i.e.* in [12] -18.0MPa) assuring that the testing method was reliable.

## 4 DISCUSSION

It is clear that the attack of OH-ions leads to the dissolution of glass in the basalt matrix and alters the microstructure of the aggregate. Arguably this fact has already been known to certain extent. However, the dissolution phenomenon has been discussed on the basis of its contribution to ASR gel formation. It was observed in this study that the dissolution phenomenon has critical influences on the strength and elastic modulus of the aggregate and indirectly on the integrity of concrete.

The microstructural study revealed that after the dissolution, remaining part is an extremely porous phase, mainly made of the remaining plagioclase crystals. This is quite obvious in the BAS_1M series specimens. Expectedly, in BAS_4M series the microstructure was even more coarsened and the remaining plagioclase crystals were also altered significantly. This probably can explain the strength difference between BAS_1M2 (the completely dissolved specimen) and the BAS_4M series. Even-though, -according to the ESEM study- they were both dissolved thoroughly, BAS_4M series exhibits lower tensile strength due to extreme alteration in the plagioclase crystals. It has been reported earlier that feldspar might contribute to the alkali budget in the system [13] but such a tremendous deterioration seems highly doubtful and far from reality considering the lifespan of concrete. Therefore it can be suggested that a realistic mechanical strength of the dissolved zone should be higher than the BAS_4M series and has a performance closer to that of BAS_1M2.

## 5 CONCLUSIONS

- Aggressive 1M and 4M NaOH solutions accelerate dissolution of glass from the basalt matrix. Authors argue that the 4M solution is somewhat exaggerated and does not reflect the characteristics of an accelerated deterioration.

- Dissolved basalt has a significantly lower tensile strength and elastic modulus in comparison with pristine basalt. The ratio is roughly 1:4. Recalculated flexural strength values of pristine and partly dissolved basalts are found to be 30-40 MPa, while flexural strength values of fully dissolved basalts are 3-9 MPa.

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TABLE 1: Summary of the specimen characteristics.

| Series | Code | Curing condition | Duration |
|---|---|---|---|
| **BAS_P*** | **BAS_P1** | - | - |
| | **BAS_P2** | - | - |
| **BAS_1M** | **BAS_1M1** | 1M NaOH solution, 80°C | 3 weeks |
| | **BAS_1M2** | 1M NaOH solution, 80°C | 3 weeks |
| | **BAS_1M3** | 1M NaOH solution, 80°C | 3 weeks |
| | **BAS_1M4** | 1M NaOH solution, 80°C | 3 weeks |
| **BAS_4M** | **BAS_4M1** | 4M NaOH solution, 80°C | 4 days |
| | **BAS_4M2** | 4M NaOH solution, 80°C | 4 days |

* pristine samples

TABLE 2: Flexural strength values of the specimens tested.

| Series | Code | Dissolved part (%) | Max[1] strength [MPa] | Max[2] strength [MPa] |
|---|---|---|---|---|
| **BAS_P** | **BAS_P1** | - | 34.1 | 34.1 |
| | **BAS_P2** | - | 33.9 | 33.9 |
| **BAS_1M** | **BAS_1M1** | 56 | 17.0 | 39.3 |
| | **BAS_1M2** | 100 | 9.3 | 9.3 |
| | **BAS_1M3** | 53 | 16.9 | 36.3 |
| | **BAS_1M4** | 34 | 21.6 | 32.4 |
| **BAS_4M** | **BAS_4M1** | 100 | 3.4 | 3.4 |
| | **BAS_4M2** | 100 | 2.3 | 2.3 |

[1]complete cross-section is considered
[2]only pristine part is considered.

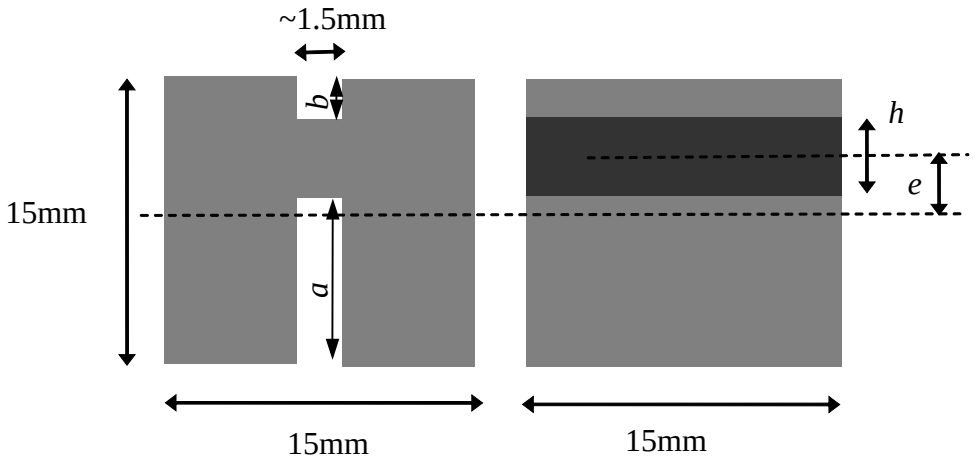


Figure 1: Build-up of a basalt specimen (non-scaled). Thickness of the cross-section (*h*), nodge depths (*a* and *b)* and eccentricity (*e*) are variable per specimen.

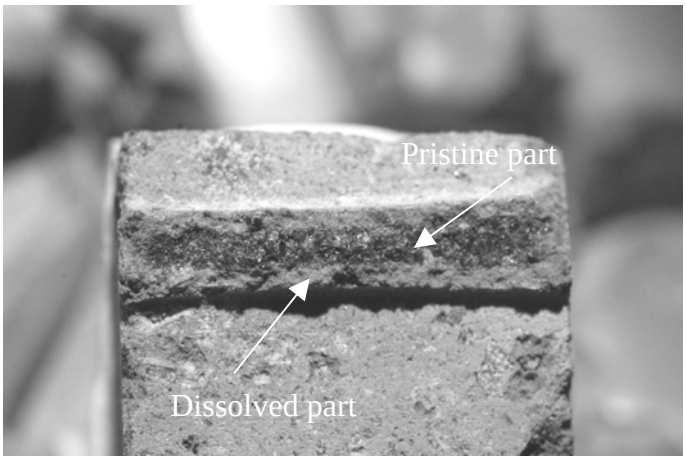


Figure 2: A broken basalt specimen. Light area at the rim is the dissolved part. Pristine basalt exhibits dark colour in the middle of the broken cross-section.

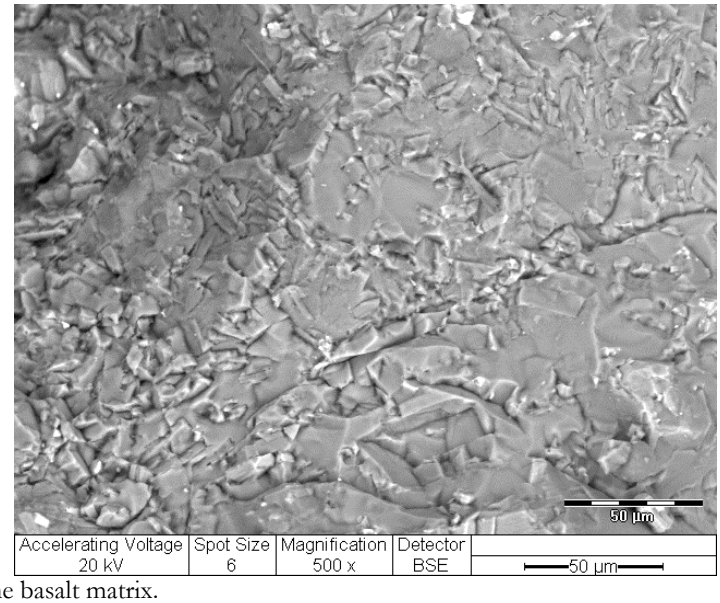


Figure 3: Pristine basalt matrix.

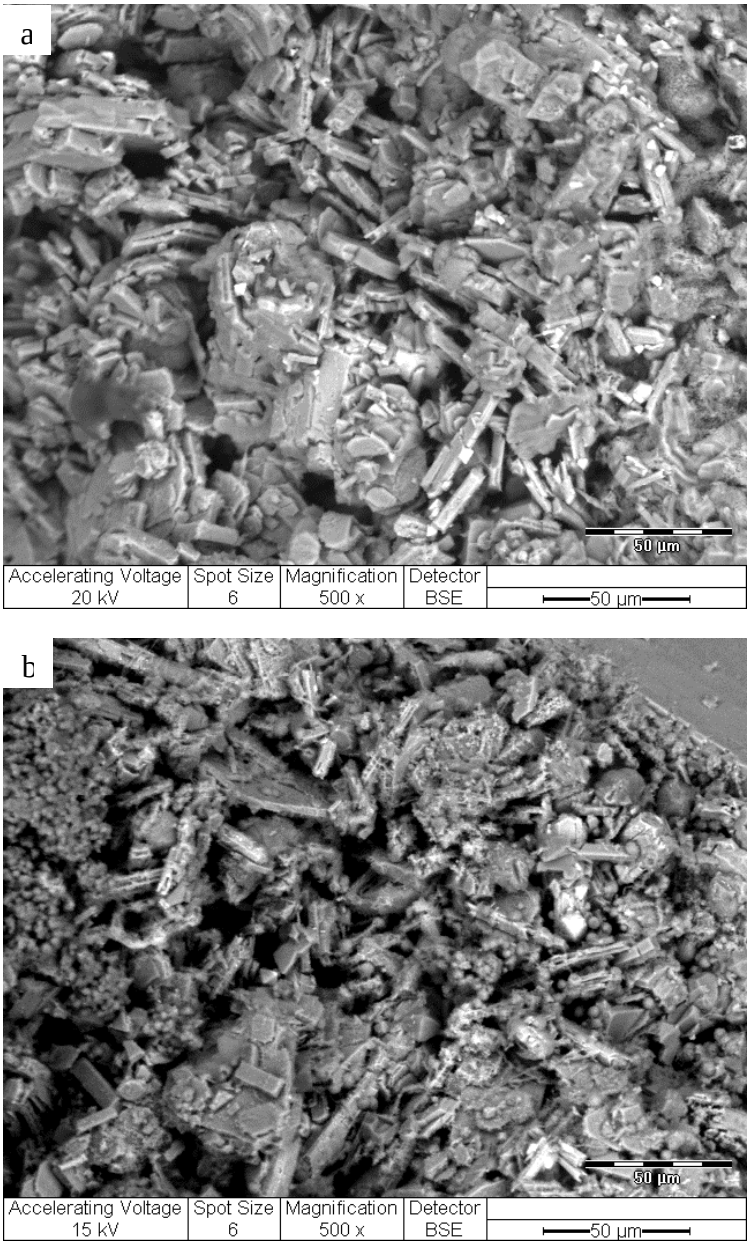


Figure 4: Basalt microstructure after attacked by NaOH solution. a) 3 weeks in 1M NaOH, b) 4 days in 4M NaOH.

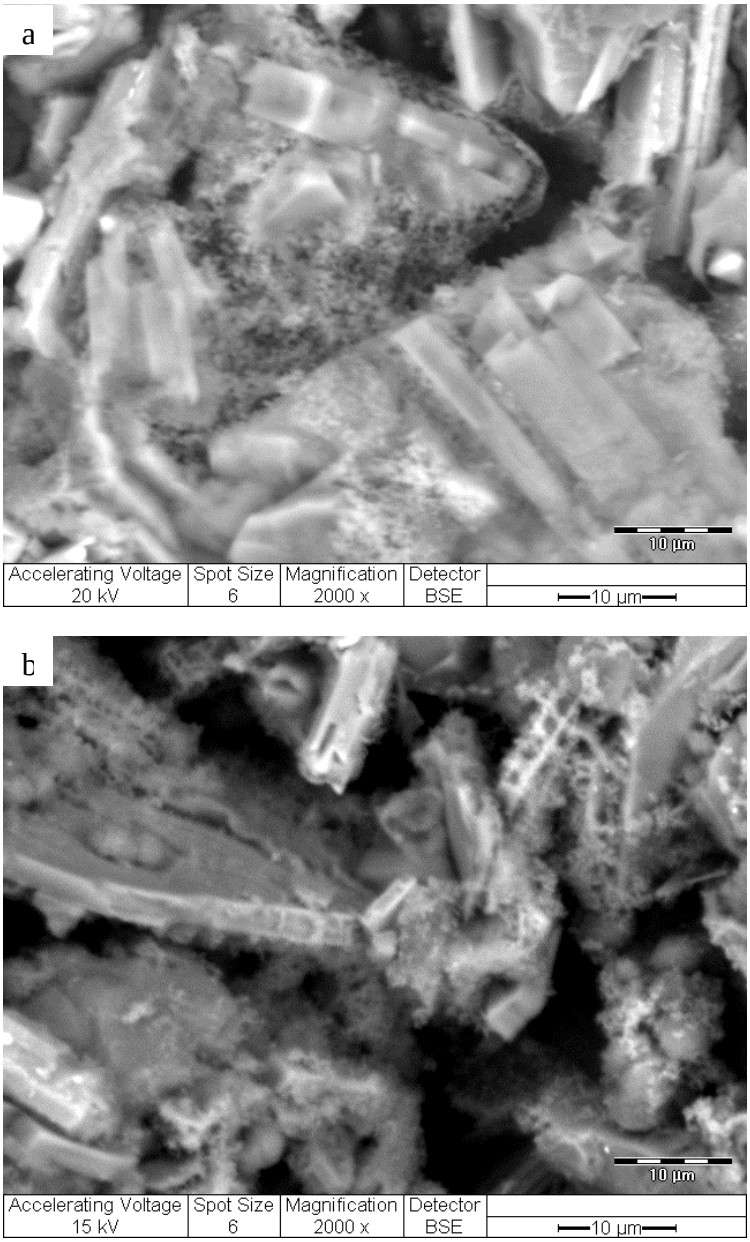


Figure 5: a) Glass dissolution around the plagioclase crystals. in 1M NaOH solution. b) glass completely dissolved around the plagioclase crystals. in 4M NaOH. Plagioclase are also affected by the highly aggressive NaOH solution.

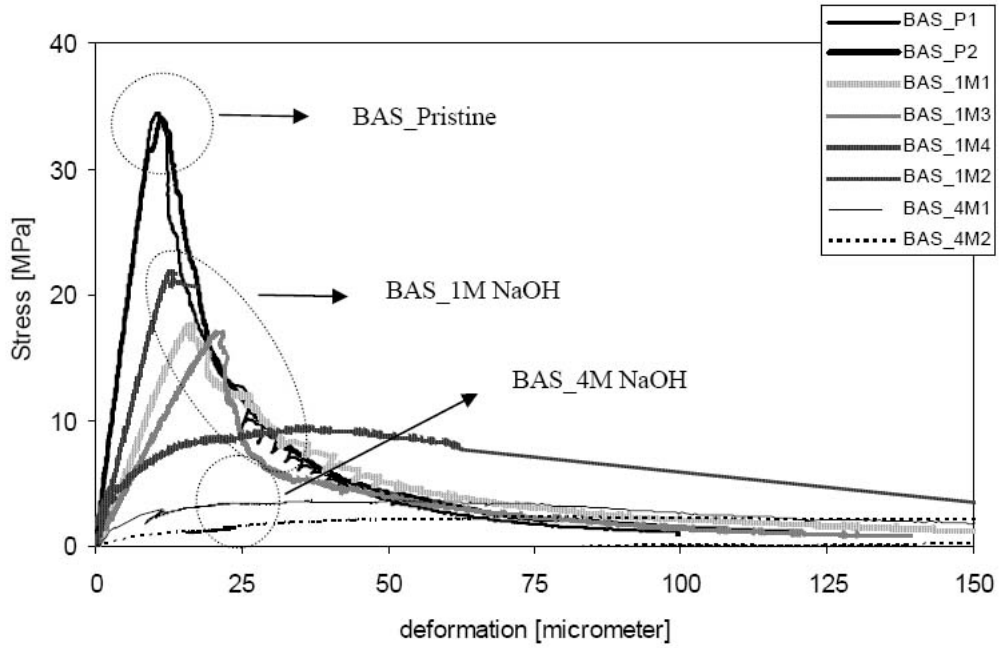


Figure 6: Stress-deformation curves of the specimens tested.

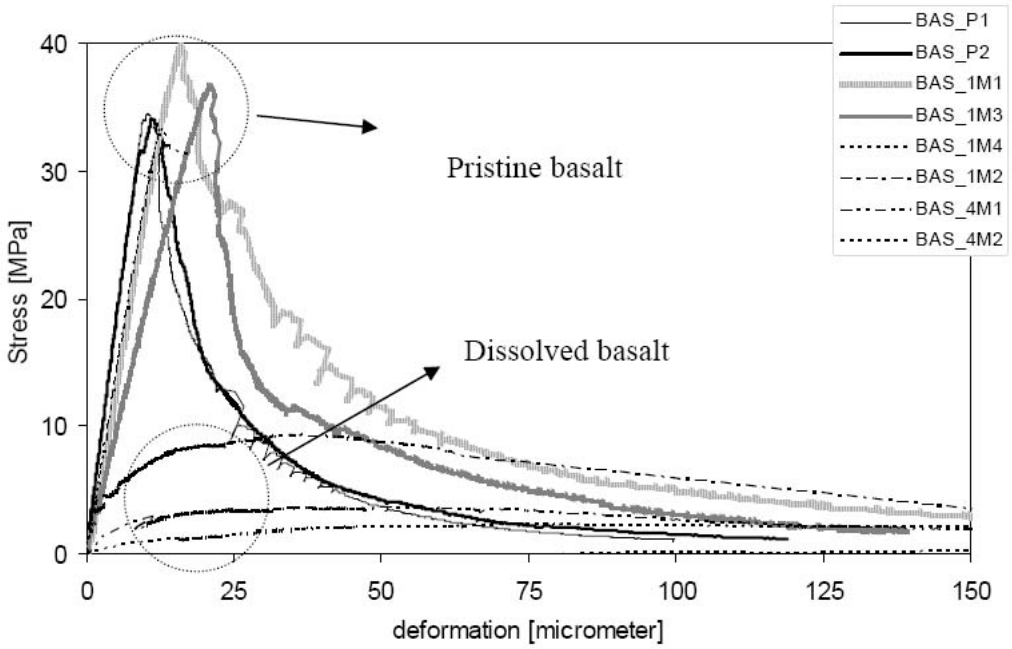


Figure 7: Re-calculated stress-deformation curves of the specimens tested.