ARTIFICIAL WEATHERING OF PORTUGUESE GRANITES
EXPOSED TO ACIDIC SOLUTIONS

M.I. Borges and A.S. Oliveira

ABSTRACT

Five types of granites [Rosa Arronches (RA), Cinzento Arronches (CA), Rosa Santa Eulália (RE), Cinzento Santa Eulália (CE) and SPI] from Portalegre (SE Portugal) have been extensively used as ornamental building stones in Portugal, and also in other countries including Japan, USA, England, Qatar, Denmark and The Netherlands. Fresh specimens of these granites were sampled from their quarries, and exposed to six, fifteen-day cycles of immersion in acidic solutions of HCl, H2SO4 and HNO3. The visual changes observed in the mineral surfaces and the mass loss percentages were monitored during the ninety days of chemical attack. Usually, HCl caused the highest mass loss and visual changes in the rock minerals, followed by H2SO4 and HNO3. The results showed that the reaction of each rock to the acidic solutions is related not only to mineralogical composition, texture, and physical properties but also to the initial state of rock weathering. The SPI granite presents the worst results, with mass loss ranging from 0.37% (for HNO3) to 0.54% (for HCl). RE granite presents the lowest mass loss, from 0.20% (for HNO3) to 0.30% (for HCl). The remaining granites present similar changes of mass loss, between 0.28% (for HNO3) and 0.41% (for HCl). Therefore, contrary to the common belief that granites are resistant to weathering by acid rain, the adoption of preventive measures when applying ornamental silicate rocks is strongly advised. Such studies can be highly useful for the ornamental stone sector companies, since improved product knowledge can boost their trade, as well as allowing competitive differentiation from their counterparts while increasing client trust.

Keywords: granite, building material, artificial weathering, acid rain

1. INTRODUCTION

Like other natural stones used for building materials, and despite the common held belief that granite as a rock is not as prone to weathering, granite is effectively susceptible to it. Thus, granites are susceptible to weather-induced decay. According to Fan et al. (2010), acid rain pollution was first observed by the British chemist R.A. Smith in 1852 and since then has attracted the attention of several environmentalists and researchers. The damage caused by acid rain in many industrialized countries in the past decades has been significant, leading to the need for expensive repairs and replacements of damaged facades.

The type and rate of weathering vary according to several factors. When thinking of the use of a natural stone as building material, it is important to consider three major factors:

a) The properties of the natural stone;
b) The climate;
c) The duration of the exposure to atmospheric conditions.

In case the exposure is long enough and atmospheric conditions are severe, even granite will chemically and physically decay [any chemical or physical modification of the intrinsic stone properties leading to a loss of value or to the impairment of use, as referred by Vergès-Belmin (2008)].
Properly using a natural stone as building material depends on knowing the characteristics that are relevant to the location and its performance in its intended use. If it will be used in the exterior of a building, for instance in slabs for cladding, the exposure to air pollution and acid rain must be considered. On the other hand, if it will be used in the interior of a building, it may be expected, among others, to suffer exposure to salt moisture, vapour, alkaline and acid products. According to I-STONE (2008), the characteristics that must be taken into account regarding its performance are: breaking load at a dowel hole, reaction to fire, and staining/cleaning. However, no standard method or acceptance criteria are presented for staining/cleaning, except that it must be reviewed by a consultant.

The role of air pollution and soiling in stone decay is a complex phenomenon, as stated by several reviewers but, so far, the emphasis of these studies has largely been on the most vulnerable rocks to acidic pollution [Doehne et al. (2010)]; thus, the studies in granitic rocks are scarce, and the Kobayashi et al. (1994) works are still a reference.

Weathering and durability are difficult parameters to quantify in granites, since both are usually based upon visual aspects or weight loss. According to Doehne et al. (2010), simple visual examination plays an important role in quantifying decay and photographic documentation is also of great value.

The main goal of the present work is to analyze the extent and identify what kind of changes might occur in the five studied lithologies when exposed to acidic solutions. In order to simulate the effects of air pollution (namely acid rain), mass loss and visual observation as parameters to quantify stone decay are used.

2. MATERIALS

The granites under study [Rosa Arronches (RA), Cinzento Arronches (CA), Rosa Santa Eulália (RE), Cinzento Santa Eulália (CE) and SPI] are primarily quarried in the southeast Portugal, Portalegre district (Figure 1) and processed by Granitos de Maceira (located in Sintra, Lisbon), which is also responsible for its national and international marketing. These granites have been widely used as ornamental and building stones, in sculpture and other applications, both in Portugal and in foreign countries.

![Figure 1: Geographic location of RA, CA, RE, CE and SPI granite quarries, marketing designation and macroscopic aspect of fresh samples [adapted from Borges et al. (2012)]](image-url)
Table 1 displays the major petrographic characteristics of the materials under study. The granites differ macroscopically due to their colour (pinkish or grey) and also in respect to the grain size and the presence or absence of a porphyritic texture. The mineralogical composition is also different in regards to the predominance of K-feldspar and plagioclase over the quartz.

<table>
<thead>
<tr>
<th>Granite</th>
<th>Petrologic description</th>
<th>Mineralogy</th>
<th>Open Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RA</td>
<td>Coarse-grained porphyritic granite slightly pink K-feldspar in a white-grey matrix</td>
<td>Microcline (40%); Plagioclase (30%); Quartz (20%); Biotite (8%); Zircon, Apatite and Opaques (2%)</td>
<td>0.42</td>
</tr>
<tr>
<td>CA</td>
<td>Medium grained blue-grey biotite granite, slightly porphyritic</td>
<td>Quartz (35%); Plagioclase (33%); Microcline (26%); Biotite (5%); Muscovite, Zircon, Apatite and Sphene (1%)</td>
<td>0.80</td>
</tr>
<tr>
<td>RE</td>
<td>Medium to coarse biotite granite with an homogeneous pinkish colour K-feldspar</td>
<td>Microcline (35%); Quartz (30%); Plagioclase (25%); Biotite (8%); Zircon, Apatite, Sphene, Allanite and Opaques (2%)</td>
<td>0.44</td>
</tr>
<tr>
<td>CE</td>
<td>Medium to fine grained biotite granite with an homogeneous grey colour</td>
<td>Quartz (35%); Plagioclase (30%); Microcline (25%); Biotite (9%); Muscovite, Zircon, Apatite, Sphene and Opaques (1%)</td>
<td>0.52</td>
</tr>
<tr>
<td>SPI</td>
<td>Fine grained monzonitic biotite granite with an homogeneous bluish grey colour</td>
<td>Quartz (33%); Plagioclase (33%); Microcline (25%); Biotite (6%); Muscovite, Zircon, Apatite, Sphene and Opaques (3%)</td>
<td>0.89</td>
</tr>
</tbody>
</table>

**TABLE 1: PETROGRAPHICAL CHARACTERIZATION OF THE SELECTED GRANITES [BORGES ET AL. (2011)]**

### 3. METHODOLOGY AND EXPERIMENTAL TESTS

In order to simulate dimension stone attack by environmental conditions, it is common to use two test types: site and accelerated tests. The first one simulates better the field conditions but requires a long period of exposure, while the second one reduces that period by using a substitute mechanism for long duration natural environment action. Therefore, in this study, like in many other studies of several authors, the second type of test was used.

The tests were performed on twenty fresh samples [three (plus one for control) for each lithology] of cubic section (60x60x10mm), each one with an approximate average weight of 90g.

The acidic solutions of HCl, H2SO4 and HNO3 were prepared with a 0.25% (v/v) concentration, corresponding to a pH of 1.16 (for HCl solution), 1.40 (for H2SO4 solution) and 1.41 (for HNO3 solution).

Before the exposure of the samples to the laboratory test, each sample was weighed, observed and its surface documented with photos. In each sample, a specific point at the surface was selected, as a reference to compare the fresh sample with the one exposed to the acidic solution.

The samples have been exposed to six cycles of acid attack; each cycle comprising fifteen days of total immersion in Petri dishes. For each cycle, the samples were retrieved from the acidic solutions, washed in deionized water, dried, weighed, visually inspected and photographed. After each cycle, the acidic solutions were also renewed. In the end of the six cycles of acid attack, corresponding to a total of 90 days, the samples were again observed and the surface changes documented with photos.
4. RESULTS AND DISCUSSION

4.1. VISUAL OBSERVATIONS

Visual observations, using a binocular stereoscope, led to the conclusion that the changes due to attack of the acidic solutions, at this scale of observation, were not very significant. However, it was observed that as conditioning continued, the surface of all the granites suffered slight damage, presenting corroded points, mostly around the dark minerals, leading to a generalized loss of brightness.

After the second cycle, the colour of the surfaces presented a slight yellow turn of the white minerals. This discolouration became more widespread after the fifth cycle of acid attack, probably due to the weathering of Fe sulphides (namely pyrite), present as accessory minerals. When in aggressive conditions, these minerals can suffer weathering leading to the formation of oxides and sulphides, which give rise to yellow-brownish (or red-brown) stains. Evidence of this sulphide oxidation and subsequent discolouration occurs because of the formation of goethite, according to the reactions:

\[ \text{FeS}_2 \ (\text{Pyrite}) + \frac{3}{2} \text{O}_2 (g) + \text{H}_2\text{O} \ (l) \rightarrow \text{Fe}^{2+} \ (aq) + 2\text{SO}_4^{2-} \ (aq) + 2\text{H}^+ \ (aq) \]

\[ 4\text{Fe}^{2+} \ (aq) + \text{O}_2 (g) + 2\text{H}^+ \ (aq) \rightarrow 2\text{Fe}^{3+} \ (aq) + \text{H}_2\text{O} \ (l) \]

\[ \text{Fe}^{3+} \ (aq) + 2\text{H}_2\text{O} \ (l) \rightarrow \text{FeO(OH)} \ (\text{Goethite}) + 3\text{H}^+ \ (aq) \]

A slight loss of the pinkish colour (in RA and RE pink granites) was also observed, due to the weathering of the K-feldspar minerals.

The flaking, micro-cracking, breakdown and loss of biotite grains and the formation of alteration products (mainly Fe oxides) were also registered in all the granites under study. The micro-cracking of the polished surfaces around the dark minerals was also observed.

4.2. MASS LOSS

The results achieved, displayed in Figures 2, 3 and 4, represent the accumulated mass loss variation in respect to each acidic solution, namely HCl, H₂SO₄ and HNO₃, for each cycle of acid attack.
FIGURE 2: ACCUMULATED MASS LOSS VARIATION OF RA (RED COLOUR), CA (DARK BLUE COLOUR), RE (GREEN COLOUR), CE (LIGHT BLUE COLOUR) AND SPI (ORANGE COLOUR) GRANITES VERSUS IMMERSION TIME IN HCl ACIDIC SOLUTION

FIGURE 3: ACCUMULATED MASS LOSS VARIATION OF RA (RED COLOUR), CA (DARK BLUE COLOUR), RE (GREEN COLOUR), CE (LIGHT BLUE COLOUR) AND SPI (ORANGE COLOUR) GRANITES VERSUS IMMERSION TIME IN H2SO4 ACIDIC SOLUTION
From Figures 2 to 4 it can be observed that:

a) All granites have presented mass loss by acid attack for all acidic solutions;
b) The mass loss was generally higher with HCl attack, followed by H₂SO₄ and HNO₃;
c) The rate of mass loss goes up gradually as the immersion time increases, for all of the granites and all of the acidic solutions;
d) The SPI and RA granites performed the poorest for all the acidic solutions, in respect to the accumulated mass loss, ranging from 0.31g and 0.32g for HNO₃ up to 0.44g and 0.43g for HCl respectively;
e) The RE granite performed the best, in respect to the accumulated mass loss, for all the acidic solutions, namely 0.28g for HCl, 0.27g for H₂SO₄ and 0.18g for HNO₃;
f) For the pink granites RA and RE, the mass loss for HCl and for H₂SO₄ attack is quite similar, with only 0.01g difference between the two solutions for both granites;
g) The CA and CE granites presented accumulated mass loss values between the RE and SPI granites values, ranging from 0.28g and 0.25g respectively for the HNO₃ acidic solution up to 0.39g and 0.38g respectively for the HCl.

The values of mass loss for the granites under study, for each acidic solution, were similar to those referred by Simão (2003). However, it can be seen that there are some differences in the behaviour of the granites under study, according to the mineralogical composition, the ratio quartz/feldspars, the grain size, the porosity and the type of acidic solution.

For pink granites, RA and RE, HCl and H₂SO₄ acidic solutions caused an almost equally significant decay. This is in accordance with the results presented by Simão (2003) for other pink granites, leading to the preliminary conclusion that in granites with higher mineralogical percentage of K-feldspar, the attack with these two acidic solutions has the same effect in respect to the mass loss. This may be due to the hydrolysis of the K-feldspar in solutions with low pH, leading to the kaolinization according to the expressions:
In general terms, it can be said that for pink granites, with higher content of K-feldspar in their mineralogical composition, the porphyritic and coarse grained RA lost the most mass (Figure 5), this being in accordance with several authors for instance Tugrul et al. (1998), who state that the grain size is the primary strength factor in granitic rocks and that the abundance of easily cleavable minerals (such as feldspars) causes a reduction in strength.

Taking into consideration the ratio of quartz/feldspars, it can be seen that the pink granites have the lowest ratios, respectively 0.28 for RA granite and 0.50 for RE granite. Furthermore, they have low values in open porosity.

With respect to the grey granites (with lower content on K-feldspar), it seems that the grain size is not a relevant factor in the decay observed, because no correlation with the achieved results for mass loss (Figure 5) can be observed. Instead, in these granites, with higher open porosity and higher content in quartz, according to Fahy & Guccione and Shakoor & Bonelli referred in Tugrul et al. (1998), the rock texture must be characterized by little intergrowth or interlocking of grains, due to the anhedral quartz grains occupying irregular spaces between the other mineral grains. In these granites, the biotite and muscovite minerals seem to contribute also to the results achieved, because of their higher susceptibility to weathering by flaking, micro-fissuring and, as a consequence, to the loss of these minerals.

5. CONCLUSIONS

The acidic solution attack tests performed lead to a generalized mass loss for all five granites. The greatest mass loss occurs with HCl, the strongest acid, followed by H$_2$SO$_4$ and HNO$_3$. The affinity of H$_2$SO$_4$ to liberate Ca present in minerals is also recognized, mainly in plagioclases.
The visual changes that occurred in the surfaces, like signs of corrosion, leaching and weathering, were common for all the granites studied.

The SPI and RA granites presented the worst results, with higher values of mass loss for the three acidic solutions.

The RE granite performed the best for all of the acidic solutions, with minor values of mass loss.

For the pink granites (RA and RE) with higher content of K-feldspar in their mineralogical composition, the porphyritic and coarse grained one (RA) performed the poorest. In these granites, HCl and H2SO4 acidic solutions caused an almost equally efficient decay.

Such evidence reveals that the effect of HCl must be considered in urban areas with high levels of pollution, since this is produced as a primary gaseous pollutant and is not dependent on the chemistry of the atmosphere for its formation. This incidence is also known in coastal areas by atmospheric dispersion of suspended sea salts.

In the grey granites, with lower content on K-feldspar, it appears that the grain size is not a relevant factor. Instead, the rock texture must be characterized by little intergrowth or interlocking of quartz grains; this, and the fact that minerals like biotite and muscovite are highly susceptible to weathering by flaking, micro-fissuring has lead to the mass loss observed.

Some signs of corrosion and weathering observed on the sample surfaces were common for all the granites: loss of brightness, yellow generalized tarnishing of the white minerals and oxidation presented in the form of brownish spots around biotite grains were observed in the grey granites. The pink granites (RA and RE) become less colourful due to the alteration of the K-feldspar, probably by the leaching of K.

The results of this study revealed the importance of considering the mineral composition, texture and structure of granites before applying them as dimension stones or as ornamental rocks. Contrary to the common belief, granites may not be resistant to weathering by acid rain. Thus, a holistic approach to the behaviour of such materials may avoid unsafe constructions and the negative economic and aesthetic impacts.

REFERENCES


