

Assessment of the potential alkali reactivity of rhyolitic rocks from Argentina

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Abstract: The potential alkali-silica reactivity of volcanic rocks of rhyolitic composition, used as concrete aggregates, was assessed focusing mainly on their petrography. Eleven samples from the Argentine Patagonia (Provinces of Río Negro and Chubut) were examined using a petrographic microscope. Thin sections were used to evaluate sample texture, degree of alteration, the presence of volcanic glass in the matrix, and metastable minerals that may contribute silica to the reaction (ASR). Results from the petrographic study were compared with those from the mortar bar test (ASTM C-1260) and the dissolved silica determined by the chemical methods (ASTM C-289).

It was concluded that rhyolitic rocks may develop deleterious reactions when they contain unweathered and/or altered glass in their matrices, and alteration minerals resulting from devitrification such as argillaceous minerals and cryptocrystalline silica. Rhyolitic rocks in which the matrix has completely recrystallized were found to be non-reactive.

Résumé: Les études pétrographiques ont été utilisées en l'évaluation de la réactivité des roches volcaniques de composition riolithique, utilisées comme agrégat pour le béton, en report à la Réaction Alcalis-Silice (RAS).

Onze échantillons provenant de la Patagonie Argentine (Province de Río Negro) ont été analysés. Le microscope de polarisation sur de lames minces a été utilisé pour l'évaluation de la texture, degré d'altération, présence du verre volcanique dans la pâte et minéraux métastables qui peuvent apporter du silice au milieu.

On a comparé les résultats de cette étude avec celles obtenues par l'essai de la barre de mortier (ASTM C-1260) et celui de la silice dissoute obtenue par la méthode chimique (ASTM C-289).

On conclut que les roches riolithiques avec de verre frais ou altéré dans les pâtes, ainsi que des minéraux d'altération provenant de la dévitrification (argilles ou silice cryptocristalline), peuvent développer des réactions délétères. Les roches riolithiques avec son matrice recristallise n'ont pas montré de réactivité.

Keywords: concrete, aggregate, rock description.

INTRODUCTION

In Argentina there are large outcrops of both acidic and basic volcanic rocks that are frequently used as concrete aggregates (crushed rock and sand). They have been employed to build major works such as dams, bridges and roads. They are also significant constituents in coarse (gravel) and fine (natural sand) aggregates. Owing to their physical and mechanical characteristics they are suitable materials for concrete manufacture, but the presence of deleterious species such as volcanic glass, cryptocrystalline silica, and expansive clays render them potentially deleterious.

In previous work, the ASR potential of basaltic rocks used as concrete aggregates was evaluated. More than twenty deposits from different provinces in Argentina were studied applying physical and chemical test standard methods. In some cases both suitable and highly reactive rocks were found within the same deposit (Maiza *et al.* 1995), (Marfil *et al.* 1998). The petrographic study was very useful for determining their potential reactivity, which was always associated with the presence of volcanic glass (both unweathered and devitrified processes) and cryptocrystalline silica (trydimite, cristobalite) in their matrices. (Marfil & Maiza 1996), (Maiza & Marfil 1998).

Rhyolite outcrops in Argentina cover large areas in the provinces of Río Negro, Chubut, Santa Cruz, Neuquén, and La Pampa. Most of them are of Triassic-Jurassic age with intrusions that extend into the Tertiary (Rapela *et al.* 1996) (Stipanovic 1967).

Glassy matrices prevail in these rocks and have sometimes developed perlitic textures, consisting of concentric cracks that impart a significant permeability to the rock and, therefore, higher susceptibility to be devitrified and then leached. The devitrification process changes glassy matrices into cryptocrystalline felsitic aggregates composed mainly of quartz or trydimite and chalcedony, abundant argillaceous minerals, other silicates and some oxides, mostly iron oxide. The predominant alteration processes are sericitization, carbonation, silicification, argillitization, and zeolitization, which strongly influence the release of silica and alkaline elements.

In Patagonia, Argentina, concrete works frequently deteriorate due to the prevailing climatic conditions such as extreme temperatures and wind action, inadequate curing of the concrete, water action, sulphate ion attack, and the deleterious reactions of aggregates (ASR). Previous studies on the alkali reactivity of rocks have shown that most of the aggregates from Patagonia are potentially alkali reactive as they result from the natural erosion or crushing of volcanic rocks with a glassy matrix (Maiza & Marfil 2003) (Maiza *et al.* 2003).

In the alkali-silica reaction there are two classes of minerals that are known to be expansively reactive with the alkalis in concrete. There are metastable types of silica and aluminosilicate glass (Katayama, St John & Futugawa 1989).

The chemical composition of rhyolites is similar to that of granitic rocks (they contain about 70 % SiO_2 and 7 % Na_2O eq.), but they have dissimilar texture (porphyritic to aphanitic), and contain phenocrysts dispersed in holocrystalline to holohyaline (glassy matrices).

From the mineralogical point of view, a rhyolite is composed of quartz phenocrysts, mostly alkaline feldspar (sanidine), albite-oligoclase, and mafic minerals—mainly biotite and hornblende. The most common accessory minerals include titanite, apatite, zircon, and iron ore, dispersed in an entirely glassy to microcrystalline matrix.

The purpose of this paper is to correlate the petrographic feature of rhyolitic aggregates with the results of other alkali reactivity tests.

MATERIALS

Eleven rhyolites from the provinces of Río Negro and Chubut (Argentine Patagonia) were studied. They have been identified as Florentino Ameghino, Villegas, Cantera 60, Cerro Alto, Sierra Chata (black and red) from the province of Chubut; and Pajalta, Don Ricardo (La Cruz and Mirador), Sierra Grande and Sierra Colorada, from the province of Río Negro. (Figure 1).

The above-mentioned outcrops belong to the Marifil Formation, of Middle Triassic to Middle Jurassic age (Rapela *et al.* 1996).

METHODS

An Olympus trinocular petrographic microscope equipped with a high-resolution video camera and software for image analysis and quantification was used to determine petrographic composition, texture, and alterations.

A Rigaku D-max IIIC, X-ray diffractometer with Cu $\text{K}\alpha$ radiation and a graphite monochromator operated at 35 kV and 15 mA were used to study alteration products in natural samples, and after being expanded with ethylene glycol or calcined. The results were compared with those obtained from previous work (Maiza *et al.* 2003) which used the standard accelerated (ASTM C227 1994) and chemical test methods (ASTM C289 1995).

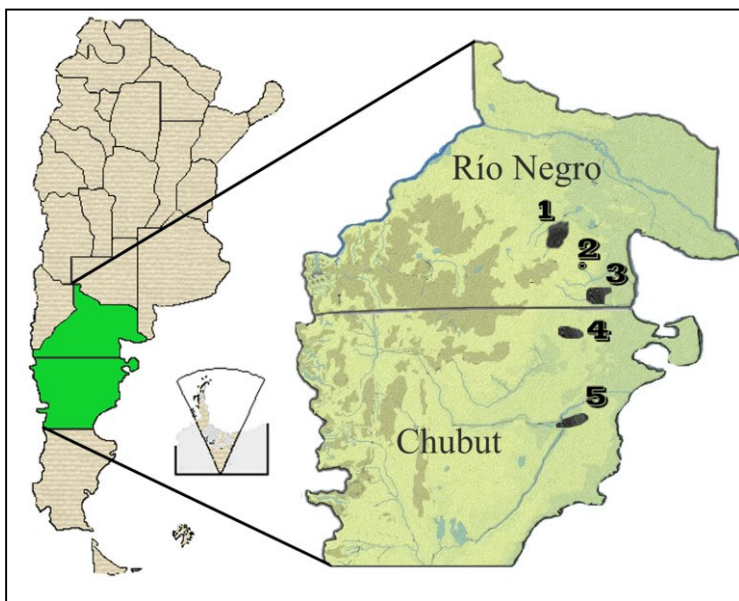


Figure 1. Location Map: 1. Don Ricardo, Sierra Colorada (La Cruz and Mirador). 2. Pajalta; 3. Sierra Grande; 4 Sierra Chata (black and red); 5. Florentino Ameghino, Villegas, Cantera 60, Cerro Alto.

RESULTS

Petrography

The analysis comprised the determination of mineralogical composition, texture, phenocryst/matrix relationship, microcrystal size, types of alteration, and presence of volcanic glass.

The Florentino Ameghino rhyolite has a microcrystalline matrix, with no glass, and the microcrystals are in the coarser range of grain size. The alteration mineral identified is illite, (Mortar bar expansion was 0.026 % at 14 days) (Maiza *et al.* 2003). Figures 2A and 2B show the mineralogical composition and texture of the Florentino Ameghino

rhyolite viewed under parallel light and crossed nichols, respectively. It is composed of quartz phenocrysts (q), sanidine, subordinate plagioclase (f), and biotite, contained in a microcrystalline matrix of fine meaning saccharoid quartz, and feldspars.

The rocks from Sierra Chata were identified as Sierra Chata black and Sierra Chata red. They were the most reactive both by the chemical and the mortar bar test methods. In the latter method they both expanded by 0.175 and 0.132 % respectively at 14 days. The matrix of the black one contains abundant glass which has been altered by argillization, zeolitization, and silicification processes; relict glass being scarce. The texture is hyalopilitic fluidal, containing abundant expansive clays. Matrix fluidity is shown in Figure 2C (parallel light). Figure 2D (crossed nichols) shows that relict glass (rg) is scarce and that a significant devitrification process has occurred. Phenocrysts are composed of quartz (q), feldspar (sanidine and plagioclase) (f), and scarce biotite.

The red rhyolite has similar characteristics, glass is abundant and shows significant alteration processes although, unlike the above-mentioned, no silicification has occurred. It has a hyalopilitic intersertal texture.

Villegas rhyolite has a microcrystalline texture, and relict glass is scarce. The matrix is coarse grained and is partially recrystallized with argillization and silicification processes. Mortar bars containing this aggregate showed no deleterious expansion (0.033 % at 14 days).

Cantera 60 rhyolite has a felsic flow texture, and the matrix is partially recrystallized. Relict glass is scarce, although the flow texture remains. Expansion of mortar bars in the ASTM C-1260 test was 0.119 % at 14 days. The matrix exhibits argillization, zeolitization, and silicification.

Cerro Alto rhyolite has a hyalopilitic texture, with a partially recrystallized matrix. The flow texture remains and abundant expansive clays, zeolitization, and silicification products have developed. Mortar bar expansion in ASTM C-1260 was 0.197 % at 14 days.

Sierra Colorada rhyolites: La Cruz and Mirador. They exhibit similar petrographic characteristics, exhibiting an intersertal texture. The microcrystalline matrix is entirely recrystallized, and no glass is present. Mortar bars expanded by 0.040 % at 14 days in ASTM C-1260 test.

Pajalta rhyolite has an intersertal texture. Minor amounts of relict glass remain. The matrix is partially recrystallized. Expansion was 0.097 % at 14 days.

Don Ricardo rhyolite has an intersertal texture, containing abundant unweathered glass. Phenocrysts are coarse (0.5 to 2.2 mm) and show signs of argillization processes (Figure 2E and 2F). Mortar bar expansion in ASTM C-1260 test was 0.139 % at 14 days.

Sierra Grande rhyolite has an intersertal texture. Unweathered glass is abundant although devitrification (argillization) and silicification products have developed. Phenocrysts are coarse (0.8 to 2.2 mm). Mortar bar expansion was 0.130 % at 14 days in ASTM C-1260 test. The results are summarized in Table 1.

Table 1. Petrography

Locality	Matrix texture	Alteration		Presence of glass
		Matrix	Phenocrysts	
Florentino Ameghino	Microcrystalline	Illite	Illite-calcite	No
Villegas	Microcrystalline - microfelsic	Argillization Silicification	Illite	Yes
Cantera 60	Felsic fluidal	Argillization Zeolitization Silicification	Illite	Yes
Sierra Chata red	Intersertal hyalopilitic	Argillization Zeolitization	Illite	Yes
Sierra Chata black	Intersertal	Argillization Zeolitization Silicification	Illite Calcite	Yes
Cerro Alto	Hyalopilitic	Argillization Zeolitization Silicification	Illite Calcite Kaolinite	Yes
Sierra Colorada Mirador	Intersertal	Argillization Zeolitization Silicification	Calcite Illite	Yes
Sierra Colorada La Cruz	Intersertal	Argillization Silicification	Illite - Kaolinite	Yes
Pajalta	Intersertal	Argillization	Calcite - Silica	Yes
Don Ricardo	Intersertal	Argillization	Illite - Chlorite Calcite	Yes
Sierra Grande	Intersertal	Argillization Silicification	Illite Silica	Yes

Dissolved silica

Representative crushed aggregate samples passing 300 and retained on 150 µm mesh sieves were used, for the determination of dissolved silica (ASTM C-289 chemical test). The results are shown in Table 2.

The results from the petrographic analysis and the dissolved silica in the chemical test method match the behaviour shown in the accelerated mortar bar test method (ASTM C-1260) for most of the samples tested (Marfil *et al.* 1995).

The effect of the degree of alteration and devitrification of the glassy matrix of volcanic rocks on reactivity is uncertain. However, extensively altered and devitrified volcanic rocks are often non-reactive (St John, Poole & Sims 1998). This inability to petrographically correlate disordered silica and altered glass with potential reactivity has resulted in a range of chemical, mortar and concrete tests being developed to determine the reactivity of aggregates (Grattan-Bellew 1989).

Table 2. Dissolved silica determined by the ASTM C-289 chemical test method

Sample	Soluble silica (mg)
Dique Ameghino	9.3
Villegas	15.9
Cantera 60	23.5
Sierra Chata, black	30.6
Sierra Chata, red	44.9
Cerro Alto	48.0
Sa. Colorada Mirador	34.3
Sa. Colorada La Cruz	39.5
Pajalta	19.3
Don Ricardo	10.5
Sierra Grande	10.8

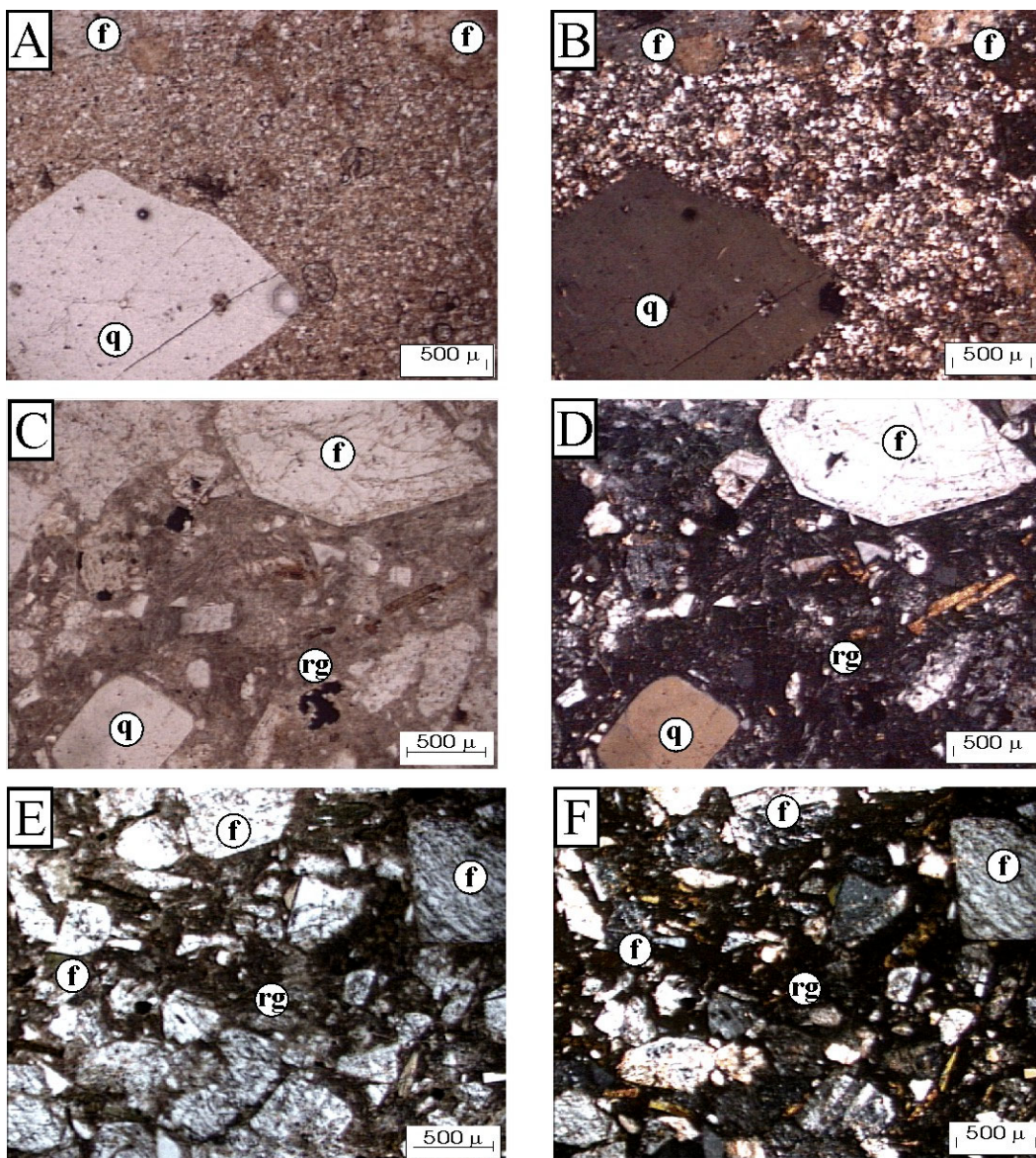


Figure 2: A and B: Florentino Ameghino rhyolite. Parallel light and crossed nichols respectively. Quartz (q) and feldspar (f) phenocrysts in a microcrystalline matrix. C: Sierra Chata, black. Parallel light. Hyalopilitic fluidal matrix. D: Sierra Chata, black, crossed nichols. q: quartz, f: feldspar. E and F: Don Ricardo rhyolite. Parallel light and crossed nichols respectively. Glassy matrix with abundant relict glass (rg). Feldspar (f) are argillized.

DISCUSSION OF RESULTS

Idorn (1961, 1967) was one of the first researchers to use thin sections to investigate the texture of reacting aggregates. Since then there have been numerous petrographic investigations of aggregate in concrete (St John *et al.* 1998).

Rhyolites that are of Mesozoic or of a later age have experienced natural devitrification processes and have significantly decreased their potential for developing deleterious reactions when they are used as aggregates in concrete.

Rhyolitic rocks have a broad time distribution from the Paleozoic to the present time. Younger rhyolites (past Tertiary) contain significant amounts of volcanic glass in their matrices, some of them being entirely glassy. The oldest rhyolites exhibit different degrees of devitrification, a characteristic that is defined by their texture, structure, and cracking. It can be said that rocks containing relict glass will be reactive. Alteration processes develop argillization forming illite, kaolinite, or zeolites with the release of silica that will appear as saccharoid quartz with a mosaic texture, if the rocks are old, and as cryptocrystalline silica or opal if they are younger.

Within the same geologic formation there are different types of rhyolites as a result of their position in the geologic environment, setting conditions, and especially the mode of cooling. For example, in the Chubut River Valley, Florentino Ameghino rhyolites, which were used to build the Florentino Ameghino dam, are entirely crystalline and therefore exhibit good performance characteristics in concrete. Other outcrops such as Cantera 60 have textures with relict glass, and that close to Villegas has altered glass, exhibiting a microfelsitic texture. The latter two rocks, whose outcrops are not over 25 km apart, belong to the same volcanism and are potentially deleterious but with distinctly different characteristics. The former is clearly reactive, whereas the reactivity of the latter can be classed as uncertain.

Among the rocks studied, crystalline rocks with recrystallized coarse-grained matrices are suitable as concrete aggregates (Rhyolites: Ameghino dam and Villegas). Those that exhibited deleterious behaviour, in the standard test methods are rocks containing relict glass, with glassy matrices that have experienced alteration processes and contain microcrystalline silica and/or chalcedony. The rest of the rocks have matrices that are composed of argillaceous minerals. These rhyolites are from Cantera 60; Sierra Chata, black; Sierra Chata, red; and Cerro Alto. Pajalta rock showed marginal behaviour in the standard tests. This is because although it still contains relict volcanic glass, most of the matrix is recrystallized.

The samples from Sierra Colorada (La Cruz and Mirador) released a large amount of silica in the chemical method but showed no expansion in mortar bars. This is due to the high microcrystalline silica content as a result of a strong silicification process. This silica is metastable and easily leachable in NaOH.

The opposite occurs in the rocks from Don Ricardo and Sierra Grande, i.e., mortar bar expansion classifies them as deleterious although they release a small amount of silica by the chemical test. These rocks contain abundant unweathered volcanic glass and coarser grain sizes. In previous work, Batic *et al.* (1986) studied the behaviour of unweathered volcanic glass in conventional test methods and concluded that relict glass would cause deleterious expansions although in the chemical method the leached silica was very scarce.

Goguel (1995) and Goguel *et al.* (2000) have investigated the alkali release from basalts and alkalinity of the pore solution in mortar and have concluded that under conditions of high humidity, large concentrations of alkalis are released from basalt. This leads to a high pore solution pH even when low-alkali cement is used (Goguel 1995) (Goguel & Milestone 2000).

Experiments have been carried out to determine the proportion of deleterious rocks in aggregates and the numerical relationships have been evaluated by computers. Hand specimen diagnosis of rock types can be misleading and is potentially dangerous. The recognition of features that might lead to reactions can only be carried out through the observations of thin section (French 2000).

CONCLUDING REMARKS

- The rhyolitic rocks studied exhibit different behaviours with respect to the ASR, depending on the volcanic glass content, texture, grain size, and degree of alteration.
- Rhyolitic rocks with entirely recrystallized coarse-grained matrices are not reactive and are suitable as concrete aggregates.
- If they contain volcanic glass that is unweathered or altered to argillaceous minerals, the glass will contribute silica and alkaline elements to the environment leading to deleterious reactions in concrete.
- Subsequent alteration products such as silicification with crystallization of minerals like chalcedony or fine quartz will render them potentially alkali-silica reactive.
- A detailed petrographic study is the first stage to decide on the suitability of this type of rock to be used as aggregates in concrete. If deleterious minerals are identified, supplementary standard tests should be conducted (chemical and mortar bar test methods).
- Rhyolitic rocks are lithologically heterogeneous, exhibit alterations and mineralogical and textural characteristics that require careful testing and analysis to predict their behaviour when they are intended to be used as concrete aggregates. It is advisable to perform different tests to see if their results are consistent in terms of ASR and therefore reliable.

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