Aqueous alteration of potassium-bearing aluminosilicate minerals: from mechanism to sustainable processing

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Aqueous alteration of potassium-bearing aluminosilicate minerals: from mechanism to processing

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The anticipated increase in demand for potassium fertilizers and alumina from developing nations experiencing high-rate of population growth brings a global sustainability concern. Most of those countries do not have economically viable resources for both commodities; and the environmental footprint of existing technologies may compromise local ecosystems. Alternatives, both in terms of resources and extraction technologies, are therefore needed. Aqueous alteration of potassium-bearing aluminosilicate minerals has been proposed as an alternative to both traditional K-fertilization and alumina production. This work discusses the mechanism of aqueous alteration of aluminosilicate minerals, and the chemical processes that have been proposed to date. Although extensive studies are found in the fields of geochemistry and materials chemistry, their results have rarely been analysed and engineered to allow a proper control and design of the chemical processing. The review suggests that such multi-disciplinary approach is required to enable the design of technologies that both comply with green chemistry principles and are economically viable.

Introduction

Inorganic fertilizers are essential for crop production, in particular to supply nutrients such as nitrogen, phosphorus, and potassium. For the later, 95% of the global production is dedicated to agriculture in the form of water-soluble salts (e.g., KCl), commonly named “potash”. Potassium content in potash varies from 50 to 60 wt. % in equivalent K_2O. Global demand of potash recently exceeded 32 million metric tons of K_2O, and a significant increase is foreseen for the coming decade[1,2]. The main ore to produce potash is sylvinite - a physical mixture of minerals sylvite (KCl) and halite (NaCl), typically with 20-30 wt.% K_2O. Few countries of the northern hemisphere (Canada, Russia, Belarus, and Germany) exploit the major rock-salt deposits and control more than 70% of the existing potash market. As far as global availability of KCl for agriculture, the United Nations Food and Agriculture Organization (FAO) emphasizes a risk of temporary shortage in the close future[3]. The reported data, presented in Figure 1 for each geographical location reveal an actual unbalance of potassium nutrient for Africa and Asia, where the difference between demand and supply is negative. A nutrient audit conducted by Sheldrick[4] pointed out that the factual demand for potash in those regions is underestimated by the FAO, and that the search for local alternative sources of potassium is already crucial for a sustainable development of those regions. In fact, FAO’s survey takes into account only the demand from the customers currently represented in the global market i.e., customers with the ability to purchase potassium fertilizer at the current price. This clearly does not include the whole agricultural community. In other words, nutrients currently removed from the soils by crop in Africa, Asia, Latin America, Central Europe, Caribbean, and Oceania are not compensated; and hence those lands are already experiencing a shortage of potassium. Their rapid population growth suggests that the situation may worsen.

Beside the limited geographical availability, traditional potash fertilizers comprise highly soluble salts, which are not necessarily the most efficient and sustainable nutrient source for all types of soils. Tropical soils, for example, typically have low cation exchange capacity and call for fertilizers with controlled and gradual rate of nutrients release. Moreover, substantial leaching of salts from agricultural field can lead to accumulation of chlorides and nitrates in ground water causing long-term environmental issues related to the sink capacity of the earth1[,5,6,7,8]. Therefore, a green alternative source of potassium needs to be earth-abundant and must allow controlled availability of K with minimal co-release of environmentally harmful elements. In that context, earth-abundant potassium-bearing rocks may offer a suitable alternative.

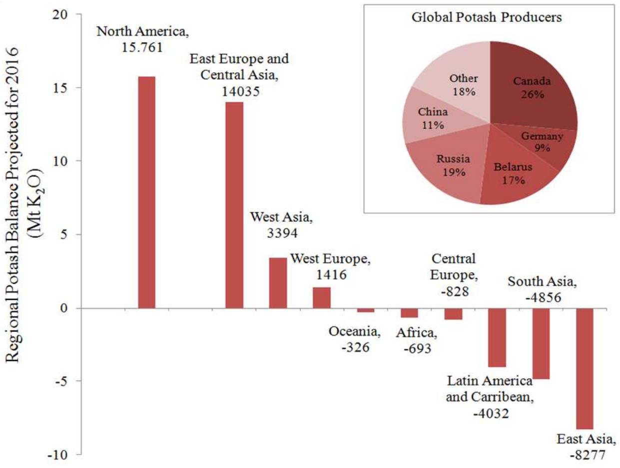

Figure 1. Projection of the regional potash balance of import vs. export according to the FAO for 2016[3] in million metric tonnes of K_2O equivalent. Inset shows the current national distribution of potash producers.

Potassium-bearing framework (tecto-) aluminosilicate minerals[*] may contain up to 30 wt.% K_2O (e.g., for kalsilite), and have been proposed as a substitute source of potassium1[,9,10,11]. In addition, their high alumina content (up to 32 wt.% Al_2O_3) might offer local alternative to bauxites – the ore used for alumina production worldwide. Al_2O_3 content in bauxites varies from 30 to 60wt.% and more than 85% of its global manufacturing (89 million tons in 2010) is consumed to produce aluminium, a commodity market in constant growth[12]. The current production of alumina from bauxite is through the Bayer process, which exhibits notoriously high energy and chemicals consumption, along with the generation of a large amount of waste of ecological concern (e.g., "red mud")[13].

However, for such products as potash and alumina the transition from a conventional to a new minerals source, in particular of lower grades, is rarely economically and ecologically acceptable using traditional extraction technologies. In other words, novel mineral sources call for novel processing approaches designed in accordance with green chemistry paradigm [14,15,16,17].

Ground K-bearing silicates ("stone-meal") were suggested as an alternative source of potassium for agriculture in the beginning of the twentieth century[18]. This approach does not involve any chemical process, and implies only crushing and grinding with minimal amount of energy (around 20kWh/t when modern grinding techniques are used). Despite its simplicity, this approach has not yet been successfully implemented in mainstream agriculture, most likely due to the slow rate of potassium release from the majority of the tested minerals[1,9,10,11,19].

Design of chemical processing to extract potassium and aluminium from earth-abundant K-bearing silicates is also a multi-century endeavour, traced back to 1856 and still pursued recently[20,21]. Two main approaches have been proposed: high-temperature (pyrometallurgy) and hydrothermal treatment. For the former, process temperature ranges between 600°C to 1400°C. Those methods require additives that form eutectics or exhibit a miscibility gap with the silicate of interest. The need for these additives (fluxes, typically salts of alkaline and/or alkaline earth metal) is a green chemistry challenge. First, the compatibility of the additive with the downstream application (e.g., fertilizer) has to be thoroughly evaluated, and second, such approach leads to large volume of by-products, which have to be disposed or recycled. Finally, quenching step, typical for such processing, requires water regeneration facilities.

Hydrothermal methods typically operate at lower temperature (150°C-300°C) and elevated pressure, and utilize water as the reagent. Hydrothermal methods aim to accelerate the natural decomposition of K-bearing silicates by aqueous fluids, a reaction that is responsible for soil formation on geologic timescale. It therefore appears particularly appropriate to discuss what knowledge has been gained from nature to design hydrothermal methods according to green chemistry principle.

Despite substantial prior art, the industrial production of alumina from non-bauxite ores is implemented only in a few countries of the former USSR[22], whereas none of those methods is currently used for potassium extraction. Earlier reviews [23,24] are focussed on the technical developments related to the transformation of K-bearing silicates into various products from 1856 to 1995. The present work is dedicated to the fundamental chemical mechanisms of aqueous alteration of K-bearing silicates, with the objective to link the knowledge available from geochemistry and materials chemistry studies. The primary objective of this paper is to demonstrate that linking of those fields is needed to identify green chemistry strategies, suitable for specific usage of earth-abundant K-bearing tectosilicates as a source of potassium and, potentially, aluminium.

The first section is a brief description of occurrence and properties of K-bearing tectosilicates. Section 2 is an analysis of the recent geochemical studies related to the aqueous alteration of K-bearing tectosilicates with primary focus on the dissolution mechanism. This section discusses the rate-controlling parameters for the dissolution and identifies the challenges related to the direct use of K-bearing tectosilicates as a sustainable substitute to potash in agriculture. Section 3 describes the hydrothermal alteration processes proposed for such minerals, focusing on the underlying chemical mechanism and the corresponding green chemistry challenges and benefits.

1. K-bearing tectosilicates as earth-abundant raw materials

In 1917, the 27th session of the British Institute of Mining and Metallurgy was devoted to "*A Neglected Chemical Reaction and an Available Source of Potash*"[25], where E. Ashcroft introduced the research related to potassium extraction form K-feldspars processed at 1000°C in the presence of NaCl, moisture and air. Arguing the practical significance, he said:

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[*] feldspars and feldspathoids later in this review named "K-bearing silicates"

"It is, perhaps, not always appreciated that feldspar is the most abundant mineral in the earth's known crust. Hatch gives us, in a striking little table in his text-book on mineralogy, an estimate of 1% for metal ores and 1% for salts, lime, magnesia, etc., and 48 % for feldspars. Potash feldspar, though, representing only one species of the feldspars, constitutes, nevertheless, a large proportion, probably, the predominant proportion, and very little consideration enables us to realize that potash, so far from being a scarce substance in nature, is really most abundant[26]".

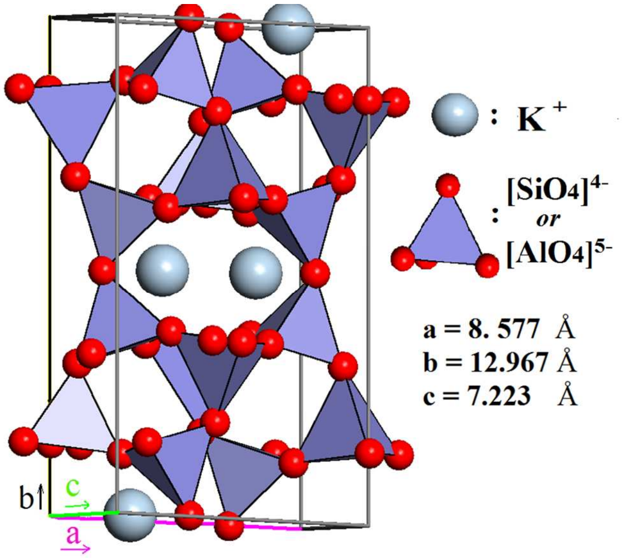

Figure 2. Idealized crystalline structure of microcline: the red spheres represent oxygen atoms; silicon and aluminum atoms are within the $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedrons, and the potassium charge-balancing cations are the blue spheres.

According to contemporary views, feldspars comprise a group of minerals that constitutes 60% of both the continental and the oceanic crusts of our planet. In particular, they are common in igneous rocks such as granites, gneisses and schists, and also occur in metamorphic, and some sedimentary rocks[27], thereby, being almost evenly distributed across liveable continents. Feldspars are crystalline aluminosilicates with the general formula $M^{1+}/M^{2+}(Al,Si)_4O_8$, often written MT_4O_8, where T stands for an element in tetrahedral coordination with oxygen. M^{1+} and M^{2+} represent an alkaline or alkaline-earth metal, acting as a charge-compensating cation. Feldspars crystal lattice is composed of corner-sharing AlO_4^{5-} and SiO_4^{4-} tetrahedra linked in an infinite 3D framework. This defines feldspars as "framework silicates" or tectosilicates (see Figure 2). The composition of pure K-feldspar ($KAlSi_3O_8$) is 18 wt.% Al_2O_3 and 16.9 wt.% K_2O, though most feldspar minerals[28] have a general formula $K_xNa_yCa_{1-(x+y)}Al_{2-(x+y)}Si_{2+(x+y)}O_8$.

The degree of ordering of Al and Si among the T-sites leads to structural transition between monoclinic and triclinic symmetries. Three polymorphs of K-feldspar have been identified by X-ray diffraction, ranked by degree of ordering: microcline, orthoclase, and sanidine. The phases observed in natural rocks are inherited from the temperature of magma solidification, its cooling rate, and their subsequent geological history[29,30]. Besides those polymorphs, a variety of terminology exists for K-feldspar-bearing minerals depending of their geological origin (e.g., "*Adularia*" from the Adula Mountains, St. Gotthard, Switzerland a low-temperature form of potassium feldspars, which structural state is nearly equally represented by microcline and orthoclase).

Feldspathoids represent another group of tectosilicate minerals with a higher potassium and aluminium content, because of their under-saturation in silica with respect to feldspars. They are more rare minerals than feldspars, though attractive in terms of potassium and aluminium extraction. Minerals Nepheline ($Na_3KAl_4Si_4O_{16}$), Kalsilite ($KAlSiO_4$), and Leucite ($KAlSi_2O_6$) are members of this group.

K-Feldspars and feldspathoids typically constitute up to 90 % of common rocks such as granites or syenites, and can form deposits of a relatively high grade, making them an abundant and locally available *reserve* of potassium and aluminium. Moreover, it is possible to find deposits that can be mined as open quarry, and not as deep-mining typical for such salts as sylvinite. The conversion of these *reserves* into *sustainable resources* however requires the development of adequate extraction technologies suitable for the foreseen materials product. From a green chemistry perspective, a promising way to achieve potassium availability from K-Feldspars and feldspathoids is to expose them to an aqueous solution by analogy with the geochemical weathering. Therefore, the following section reviews the most recent geochemical studies related to the mechanism of aqueous dissolution of these minerals, using K-feldspars (later named KFS) as the paragon of K-bearing tectosilicates).

2 Dissolution mechanism of K-bearing silicates, as derived from geochemical studies

Chemical weathering is the natural process of mineral alteration mediated by fluid, which results in the replacement of primary rock-forming minerals by secondary minerals, more stable under the given conditions[31,32]. During weathering, several reactions occur simultaneously at the mineral-fluid interface as schematically shown in Figure 3.

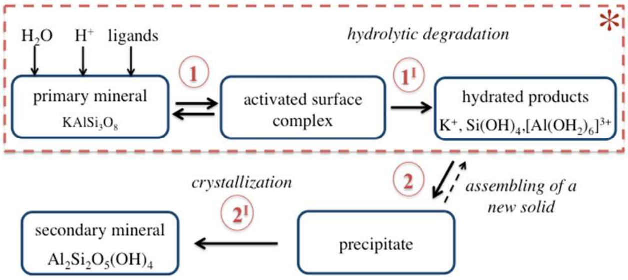

Figure 3. Schematic of aqueous alteration of K-bearing framework aluminosilicates and scope of the present review (*). During dissolution (marked by the dotted line), the reactants form a metastable activated complex on the mineral surface (step 1^1). The chemical nature and composition of the species contained in the fluid determine both the complex and hydrated products to be formed after the irreversible decomposition of the mineral (step 1^1). For instance, silica and alumina hydrates shown in this schematic exist at pH ≤ 3. The formation of a new solid may involve precipitation of a metastable intermediate (step 2) followed by structural and compositional changes (step 2^1), which lead to the formation of secondary crystalline phases.

Dissolution of K-bearing silicates involves release of charge-balancing cations (e.g., K^+) via ion exchange, adsorption/desorption of dissolved species at the mineral surface exposed to the fluid (step 1 in Figure 3), and hydrolytic degradation of the T-O-T linkages (step 1^I in Figure 3). The ultimate step is the removal of hydrated alumina and silica species from the crystal lattice (see Figure 4). A new solid phase is formed along the dissolution profile due to the assembly of metastable precipitates, followed by nucleation, growth, and recrystallization of a secondary mineral (steps $2\text{-}2^I$ in Figure 3).

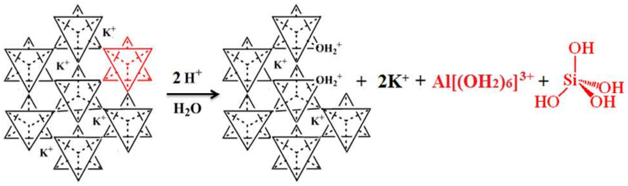

Figure 4. Schematic of proton-promoted dissolution of K-bearing tecto-aluminosilicates, illustrating the dissolution of one cluster. The tetrahedrons can contain Si or Al

In geological systems, molecular flow in the vicinity of a mineral surface is often space-constrained, which causes local oversaturation of aqueous silica, alumina, and other ions. The surface of a primary mineral offers a lower energy barrier for nucleation, thereby serving as a substrate for the precipitates. New phases therefore appear preferentially at the fluid-mineral interface, starting the propagation of the weathering profile at the macro-scale[33,34,35].

At low fluid saturation, the dissolution rates obtained for K-feldspars at room temperature in acidic solutions (pH range 1-5) in laboratory vary from 10^{-13} to 10^{-10} $mol_{KFS}.m^{-2}.s^{-1}$ [36]. The rates *observed* on geological sites are typically 10-3000 times slower[37,]. This inhibition of mineral dissolution in natural fluids is attributed to high saturation states of these fluids, formation of secondary phase at the fluid-mineral interface, seasonal temperature fluctuations, and partial wetting of mineral surface[38].

The focus of the present work is the mineral alteration aimed at increasing the availability of potassium and aluminium. Therefore, only the highest dissolution rate, i.e., corresponding to the dissolution under low fluid saturation states, also named "*far from equilibrium dissolution*" is discussed below (see dotted area in Figure 3). The precipitation of a secondary phase from oversaturated solutions is therefore not addressed.

Many studies prior to 1980's referred to solid-state diffusion through a partially altered surface layer as the rate-determining step in the dissolution of rock forming silicate minerals[39,40,41]. Later, this diffusion-controlled model has been reconsidered, and surface reactions at the fluid-mineral interface (namely, the detachment of a surface complex illustrated by step 1^I in Figure 3), has been proposed as the rate-limiting step[42,43]. Recently, high-resolution transmission electron microscopy has been extensively used to examine the surface of Ca-feldspars during acidic dissolution[44]. A step-like change in Ca, Al and Si concentrations registered in the pre-surface layer has been reported at the nanometer scale. Such abrupt concentration profile is considered as incompatible with the diffusion-controlled dissolution model, but rather suggests an interfacial dissolution-re-precipitation mechanism: "*Non-stoichiometric dissolution is limited to a layer of few unit cells, and may result in re-polymerization of silica fragments when dissolution rate of amorphous silica is slower than net mineral dissolution rate*"[35].

Based on considerable experimental and theoretical work, the net dissolution process has been expressed as the following series of elemental chemical acts (see also Figures 3 and 4):

1. Ion-exchange (proton ↔ charge balancing cation), *fast and reversible*;
2. Surface + water molecule ↔ surface species, *fast and reversible*;
3. Surface species → dissolved species, *slow and irreversible*.

However, this scheme does not distinguish the role of the network-forming elements (Al and Si) in the formation of a surface complex. A series of studies over a broad range of pH showed distinct reaction mechanisms for different surface entities (e.g., Al–O–Si and Si–O–Si)[45,46,47]. For instance, *ab initio* molecular orbital (MO) modelling of Al transition from 4- to 6-fold coordination state at the feldspar-water interface in acidic pH has been proposed. This model combined with cross-polarization magic angle spinning ^{27}Al solid-state nuclear magnetic resonance (CPMAS-NMR) demonstrates the formation of 6-fold coordinated aluminium ion "*on the feldspar surface prior the ion release in the aqueous phase*"[48]. This feature distinguishes the dissolution behaviour of aluminium in aqueous fluids from the other ions that constitute K-bearing aluminosilicates.

It should be also emphasized that far from equilibrium dissolution rates measured in laboratories are typically referred to "*steady-state*" dissolution, though the rates often do not reach constant values[49]. In other words, no plateau is reached for potassium, aluminium, and silicon concentration as functions of time in most of the flow experiments with fine-ground minerals[50]. For example, the rate of Si-release from plagioclase feldspar observed after 200 days was between 1.5 and 4.10^{-12} $mol.m^{-2}.s^{-1}$ at pH=5 and 25°C, but decreased to 2.10^{-14} $mol.m^{-2}.s^{-1}$ after 3.7 years[51] ((see Figure 5). This phenomenon can be explained by variations in surface area and roughness during long-term leaching experiments. Another explanation may be the reduced driving force for the release of Si and other elements once the fluid is approaching saturation with respect to the corresponding ions[52]. The longest experiment reported to date (> 6 years) reveals that freshly crushed plagioclase had not reached steady-state dissolution within such a timeframe. In contrast, the laboratory dissolution of naturally pre-weathered granite exhibited relatively constant rates after several months only. Nevertheless, the term "*steady-state dissolution*" is used to describe the period when the rate of mineral dissolution stabilizes at a quasi-constant value.

Whilst the details of the dissolution mechanism remain a subject of research, the experimental dissolution rates measured in laboratory for K-bearing silicates, and particularly K-feldspars, are fairly well established. On a geological time scale, these rates are affected by large-scale dissolution/re-precipitation events, which ultimately drive the genesis of sediments, soils and landscapes, determine soil fertility and the composition of ground water[53,54]. On the industrial and agricultural time scales, however, the low-temperature dissolution of K-feldspars and feldspathoids in non-aggressive aqueous fluids is prohibitively slow: the mean life of a 1-mm crystal of K-feldspar and nepheline in exogenic cycle are 520,000 and 211,000 years, respectively[55].

This reality points out to the need to design a chemical medium more efficient than weathering fluids in order to accelerate the release of the ions of interest from K-bearing aluminosilicate minerals. High acidity (resp. basicity), organic and inorganic ligands, and the presence of various defects in minerals lattice can accelerate the dissolution rate in aqueous fluids. These and other factors, crucial for the design of a green chemistry process and the effective use of K-bearing silicates, are reviewed in the forthcoming sections.

2.1. Far-from-equilibrium dissolution in aqueous fluids

2.1.1. Effect of pH and inorganic ions

It has been proposed that the dissolution rate of feldspars and feldspathoids is a function of protonation of alumina. The surface charge of alumina groups, predominantly positive ($\equiv Al\text{-}OH_2^+$) in proton-promoted dissolution and negative ($\equiv Al\text{-}O^-$), in hydroxyl-promoted dissolution, varies in acidic and basic fluids respectively. The influence of protonation of ≡Si-OH and bridging ≡Si-O-Si≡ surface sites is not to be discounted as well[56,57,58,59].

Figure 5 depicts the net dissolution rate of K-feldspars and feldspathoids with respect to pH. The rate is reported to increase with decrease in pH lower than 4; it is almost pH independent near to neutral region; and increases with an increase in basicity for pH greater than 8.

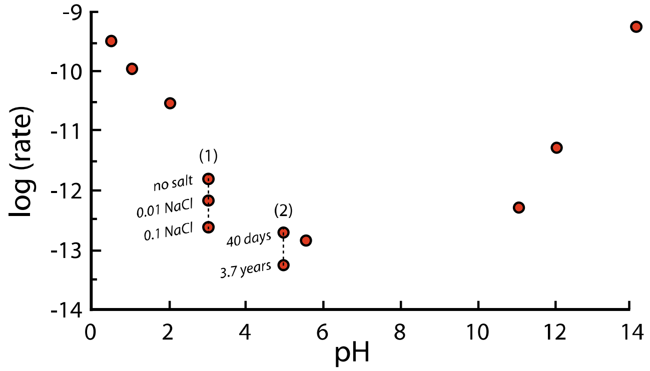

Figure 5. Effect of pH on far-from equilibrium dissolution rates of K-feldspars in ambient conditions; (1) effect of ionic strength at constant pH of the fluid; (2) effect of leaching time at constant pH of the fluid

For pH lower than 4, the rate law can be written as following:

$$R_H = k_H^+ \cdot a^n \qquad (1)$$

where, k_H^+ is the proton-promoted dissolution rate constant that ranges from 10^{-10} to 10^{-8} $mol_{KFS}.m^{-2}.s^{-1}$, and *a* is the activity of H^+, raised to the power n.

Likewise, for pH greater than 8:

$$R_{OH} = k_{OH}^- \cdot b^m \qquad (2)$$

where, *b* is the activity of $[OH^-]$, and k_{OH}^- varies from $10^{-10.43}$ to $10^{-7.33}$ $mol_{KFS}.m^{-2}.s^{-1}$.

Estimates of n and m vary from 0.4 to 1 and 0.3 to 0.7, respectively[34]. In equations (1) and (2), n and m encompass the influence of intrinsic properties of the minerals such as crystal imperfections that accumulate an excess of free energy. More generally, the dissolution rate as a function of pH is expressed using a pseudo first-order approximation, as follows:

$$R_{pH} = k\, S_c \qquad (3)$$

where, S_c is the surface charge ($mol.m^{-2}$) that can be estimated by surface titration[42,59], and k is an apparent rate constant (s^{-1}). The surface charge value obtained for albite varies from $10^{-4.25}$ to 10^{-6} $mol.m^{-2}$ in the pH range 2-11, with a minimum in the vicinity of neutral pH; whereas k is typically $10^{-6.5}$ and $10^{-6.1} s^{-1}$ for acidic and basic solutions, respectively[58].

However, usage of large amounts of strong acids/bases for extraction is a serious environmental challenge, because such reagents have to be synthetized, and possibly regenerated. They also require reactor materials that are compatible with such harsh medium, most which have a significant environmental impact during their extraction (e.g. titanium).

2.1.2. Effect of surface preparation

Since the surface concentration of specific active sites (S_c in equation 3) can be directly measured in a broad pH range, the rates derived from surface speciation model usually match laboratory data obtained for an identical sample. However, besides pH, inhomogeneity of mineral surface also leads to variations in S_c. This effect might be caused by bulk intrinsic inhomogeneity of a mineral or sample preparation such as surface roughness and lattice distortions induced by grinding. Analogous to the modification of the isoelectric point of silica induced by mechanical treatment - up to 0.4 units and higher[60] - S_c measured for K-bearing silicates also varies depending on the powder preparation method. The role of surface charge seems to be even more critical when one considers water molecules dynamics in the vicinity of an oxide surface: water ability for dissociation and subsequent proton transfer are highly affected by the surface properties of the solid phase[61,62]. Dove and co-workers demonstrated the surface-control of solvent reactivity for SiO_2 polymorphs[63,64], but this information is not available for most of K-bearing silicates. Moreover, it is still unclear, which functional groups form at the fluid-mineral interface at different stages of the dissolution process and how their interactions with water molecules modify the surface chemistry in various pH ranges. This information might be crucial, however, to design novel green extraction schemes. A mechanical pre-treatment of the minerals is indeed an appealing method from a green chemistry perspective, e.g. mechanoactivation[65,66] or ultra-sound treatments[67].

2.1.3. Effect of inorganic ions

Besides pH, mineral dissolution rate is also sensitive to competitive absorption of dissolved species other than H^+/OH^-. Natural fluids often contain inorganic ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, Al^{3+}, and more complex polynuclear ions of alumina and silica as well as anionic species that play a role in the dissolution of silicate minerals[68,69,70, 71]. Contrary to the hydrolysis of silica, where alkali cations can weaken the Si−O bonds, and, thereby, promote hydrolysis[62,72,73,74] the rate of dissolution of feldspars in acidic to near-neutral pH decreases with increase in the ionic strength of the fluid. For instance, K-feldspar dissolution rates (T=25°C, pH=3) measured in flow reactors with an influent containing 0.01 and 0.1 $mol.l^{-1}$ NaCl were $7.15.10^{-13}$ and $2.59.10^{-13}$ $mol_{KFS}.m^{-2}.sec^{-1}$, respectively. Interestingly, the rate observed in the same reactor but in absence of foreign ions, was as high as $1.63.10^{-12}$ $mol_{KFS}.m^{-2}.sec^{-1}$ (Figure 5). Competition of foreign ions with H^+ in acidic fluids for the exchange sites on mineral surface is put forward to explain this observation[68]. The fact that cations with relatively large hydrated size (e.g., $(CH_3)_4N^+$) exert a lower inhibition on the dissolution rate is in good agreement with this hypothesis. However, it has been demonstrated[75] that the hydrated size of a cation is not the only parameter determining the cation-exchange selectivity of aluminosilicate surface, and that the stability of ≡T-O-M and ≡T-OH surface complexes should also be taken into consideration[76].

Aqueous silica and alumina speciation have been extensively studied in the field of sol-gel chemistry [62,77,78], and the role of framework-forming elements at concentrations below solubility line deserves attention for mineral dissolution studies as well. Oligomerization of silica in undersaturated solutions (4, 12, and 21 $\text{mmol}_{SiO_2}.l^{-1}$) was studied as a function of ionic strength (0.01-0.24 M_{NaCl}), and pH 3-11, at 25°C using colorimetric silicomolybdate method[79]. This study supports the hypothesis that natural fluids undersaturated in respect to SiO_2 may slowly approach steady-state equilibrium with respect to amorphous silica, and thereby, inhibit mineral dissolution. From a green chemistry standpoint, not much flexibility is offered on the choice of the inorganic ions for K-feldspar processing, in particular for fertilizers, as the use of alkaline (Na^+) has to be strictly controlled for agronomic applications. Some micronutrients elements could be considered as acceptable (e.g., Fe, Mn, Mo, and Zn.) though the concentration/cost/benefits still remain to be quantified.

2.1.4. Ligand-promoted dissolution

In addition to the critical role of pH, dissolution of aluminosilicate minerals can be modified by a variety of organic ligands. The dependence of the dissolution rate on the nature and the concentration of ligands has been extensively studied[80,81,82,83,84,85,86]. Organic acids with anionic groups capable of complexing aluminium provide both ligands and proton that participate in the mineral degradation. The rate law for acidic dissolution of feldspars in the presence of a ligand is proposed to be the sum of proton- and ligand-promoted rates:

$$R_t = R_H + R_L \qquad (4)$$

where R_t is the overall dissolution rate, R_H and R_L are proton-promoted and ligand-promoted rates, respectively. By analogy with R_H, R_L is expressed as $k_L.a_L^m$ where k_L refers to the ligand-promoted rate constant, and a_L is the activity of the ligand (L)[87]. Dissolution rates for feldspars have been evaluated at 25°C in pH 3-7 with oxalic acid in concentration ranging from 0-8 millimoles per liter [88]. It has been suggested that pure ligand-promoted rate is a function of the activities of $HC_2O_4^-$ (bioxalate) and $C_2O_4^{2-}$ (oxalate), and may be expressed as:

$$R_t = 10^{-12.8}(a_{HOX}^{-}+a_{OX}^{2-})^{0.75} \qquad (5)$$

where, a_{HOX}^- and a_{OX}^{2-} are the activities of $HC_2O_4^-$ and $C_2O_4^{2-}$, respectively.

Organic ligands can therefore enhance the dissolution rate of feldspar in acidic conditions up to 15 times. The increase of surface area of the feldspar powder during dissolution in oxalic acid, determined to be of one to two orders of magnitude, has however not been taken into account in this evaluation. Aside from this surface area increase, it has been observed that ligand-promoted dissolution is also dependent upon the degree of Al–Si ordering in K-feldspars[89]. A 5-fold increase in the cumulative Si concentration was observed after 75h with respect to the dissolution in absence of organic ligands for highly disordered sanidine; whereas 90% increase was reported for highly ordered albite. It should be emphasized that this study was designed to replicate the conditions of geologic carbon sequestration (P_{CO_2}=100atm, T=90°C, 0.1M_{NaCl}, initial pH=3.1, oxalate/acetate concentrations 0,0.01 and 1M). In those conditions, both ligands enhanced the net rate of dissolution, though oxalate showed a more prominent effect than acetate.

The corresponding rate is also influenced by the aluminum/iron content of the mineral. In pure synthetic aluminosilicates, aluminum is the only element prone to complexation, whilst the feldspar-bearing rocks always contain other complex-forming elements, e.g. iron. Aluminum and iron form stable coordination complexes with hard Lewis bases such as OH^-, F^-, PO_4^{3-} SO_4^{2-}, $C_2O_2^{2-}$, CH_3COO^-, ROH, RO^- or RNH_2. The most stable complexes are obtained with multidentate ligands with negative oxygen electron-pair donors[90]. This organo-mineral interaction mediated by fluid constitutes the chemical basis of bio-weathering, where both proton-promoted and ligand promoted mechanisms might be involved. Other parameters being equal, the efficiency of carboxylic anions of low molecular weight for dissolution of silicate minerals has been ranked as following: citrate≥oxalate>maleate.

In the context of agricultural application of K-bearing silicates, the effect of organic ligands might be considered as a *soft* processing approach. The usage of organic acids available in nature (e.g., substances produced by plants, fungi, and bacteria) is one possible approach that may alleviate the reliance on inorganic acids[91]. In particular, organic acids can modify their binding properties with minor pH shift, which at large scale implies a lower consumption of inorganic acids or base. Such soft chemistry approach could ultimately help to reduce waste production during the downstream recovery of K or Al. Clearly, a better understanding of organic acids might pave the way for the design of green chemistry methods of potassium extraction, in particular for agricultural needs, as discussed in section 2.2

2.1.5. Effect of temperature

For feldspars, the net dissolution rate typically increases by about two orders of magnitude with an increase in temperature of 100°C in the range 25-300°C at constant pH. For albite, an increase from 10^{-12} (25°C, pH=3) to 10^{-6} $\text{mol}_{KFS}.m^2.s^{-1}$ at (300°C pH=3) has been reported[92]. Generally, the temperature dependence of a reaction constant (k) is expressed by an Arrhenius equation:

$$k = A \exp(-E_a/RT) \qquad (6)$$

where, A is the pre-exponential factor, and E_a the activation energy; R the gas constant; and T the temperature in degrees Kelvin. But, the difficulty in applying equation (6) to feldspar dissolution is that the dependency of the dissolution rate on temperature is affected by pH of the dissolving fluid and vice-versa. For instance, an increase in temperature at constant pH leads to an enhanced cation/decreased anion adsorption on oxides (Al_2O_3, Fe_2O_3, TiO_2, and feldspars). This reality exacerbates the effect of acidity on the dissolution rate[93,62]. Therefore, an Arrhenius expression for the dissolution of aluminosilicate minerals is valid only within a given pH range and, more generally, for a constant composition of the fluid[94,95]. The temperature and pH dependences for albite dissolution in acidic fluids have been derived from experimental data using Arrhenius-like model[96]:

$$\log R = -2.71 - 3410/T - 0.5pH \qquad (7)$$

This equation is valid in the 5 – 300°C temperature and 1-5 pH ranges. The net activation energy is proposed to be equal to 65kJ $.mol_{KFS}^{-1}$ and independent of pH. According to this model, the maximum dissolution rate for albite at pH=1 and T=363K (90°C) is $2.34 \cdot 10^{-09} mol_{KFS}.m^2.s^{-1}$. Generally, for feldspars and feldspathoids, the variation of the logarithm of the rate with pH at elevated temperatures displays a U-shape[92,97] similar to that for ambient temperature represented in Figure 5.

The operational standard molar activation enthalpies ($\Delta H_{app} = E_a$-RT) for K-feldspar are typically obtained in experiments where temperature is changed and all other parameters are kept constant; significant amount of such data are gathered in the Arnorsson and Stefansson's paper[98]. In earlier literature, ΔH_{app} varies to a high extent: from 19 to $200kJ.mol_{KFS}^{-1}$[34]. Such a broad range is caused by differences in experimental conditions or approaches of kinetic modelling. For instance, study 99 performed for albite and adularia at 25 - 200°C reported apparent activation enthalpies of 80 and $37kJ.mol_{KFS}^{-1}$ for low and neutral pH respectively. Another study for albite performed at 25 and 70°C reported values of 119, 54, and 32 $kJ.mol_{KFS}^{-1}$ for acid, neutral and basic pH, respectively[100].

In spite of such discrepancies, ΔH_{app} proposed for feldspars dissolution in acidic fluids are reproducibly higher than those for neutral pH. On the contrary, activation energies calculated from the slope of Arrhenius plot shall exhibit the highest value for the slowest reaction (here, the neutral dissolution), if the reaction mechanism does not differ. Surprisingly, such deviation has not been particularly addressed, and might be an indication of a greater temperature dependence of the rate-limiting reaction in acidic conditions, meaning that the reaction mechanisms in acidic and neutral pH are different. In this context, the higher empirical ΔH_{app} values calculated for strong acidic pH are compensated by a higher pre-exponential factor (A). Variation of A with pH, in turn, can be discussed in the context of pH dependency of surface concentration of sites potentially available for complex formation. As mentioned in section 2.1.1, feldspar surface charge has the lowest values at neutral pH and increases linearly with decrease in pH[59]. Such increase in surface charge promotes hydrolysis by reducing the energy barrier for proton transfer to the transition state[101], and might be driven by the protonation of oxygen atoms located in the bridging hydroxo groups on the surface. Therefore, one can speculate that the pre-exponential factor A for data obtained at a given pH and fitted to an Arrhenius model reflects the surface concentration of sites potentially available for complex formation, which, in turn, varies with fluid acidity.

The temperature leverage to accelerate the rate of leaching remains extremely powerful at the process level, and may be compatible with a green-chemistry approach. For instance, the targeted range of temperature for hydrothermal treatment of K-bearing silicates remains relatively low - 100 to 300°C (see section 3) opening the possibility to use waste heat from other high-temperature process.

2.1.6. Crystallographic control and future directions for dissolution studies

As mentioned in 2.2.1, various crystal defects, both intrinsic and introduced by sample preparation affect mineral dissolution kinetics. Surface inhomogeneity at sub-micron to atomic scale might be caused by bulk inhomogeneity of a geological origin (e.g., textural imperfections, recrystallized areas, rock microstructure, etc.) or by sample preparation (e.g., surface roughness and lattice distortions induced by grinding). Surface inhomogeneity affects the mineral surface charge and, hence, the pH dependency of its dissolution rate (see section 2.2.1). In addition to defects, preferential dissolution along particular crystal planes has also been reported for many minerals, including feldspars[102,103,104]. Despite experimental evidence of the crystallographic control of minerals dissolution, none of the models reviewed in section 2.1 quantify this effect.

It should be noted that there is also a lack of methods to predict the extent of lattice distortion (sometimes called *amorphization*) of mineral surface caused by different grinding techniques. Laser- and gas adsorption analysis provide important information about particle size distribution and specific surface area of a mineral powder – parameters that are typically taken into account in dissolution studies. However, the influence of the duration and method of grinding on the dissolution cannot be quantified with only those two parameters. Factors such as Fe-poisoning introduced by steel-containing milling media, non-cumulative particle size effect (e.g., particles of sub-micron size dissolves relatively faster than those of microns size, regardless of cumulative surface area), mechanically-induced lattice distortions, etc. can have a key influence on the dissolution kinetics, especially in short-term dissolution experiments.

The role of structural defects in mineral dissolution kinetics, often covered under the term microstrain, has been integrated in a stepwave model (DSM)[105,106]. This model takes into account surface topography and attempts to link far-from-equilibrium dissolution rates with those derived from near-equilibrium studies. In other words, DSM is aimed at integrating the atomic scale mineral/fluid interaction with bulk dissolution experiments and macro-scale geochemical observations. One possible method to observe the evolution of reacting surfaces with atomic resolution suitable for validation of DSM model is vertical scanning interferometry (VSI), which provides nanometer vertical resolution, and 0.5-microns lateral resolution[107].

Most of the mechanisms reviewed in this section have been derived from bulk dissolution experimental data combined with post-immersion solid phase characterization or ab-initio modeling[76]. However, a gap exists between the rate law derived from dissolution experiments and molecular simulation. Better understanding of far from equilibrium dissolution kinetics could be obtained by quantifying the effect of surface defects and nanometer-sized aqueous intermediates formed on the mineral surface. Combining modern spectroscopic methods[108,109] with computational simulations is a critical endeavour. Such investigations can help to identify elementary reactions that take place on the mineral surface, and ultimately describe pH-sensitive competitive ion adsorption, the role of crystallographic orientation of dissolving planes and the inhibiting/promoting effect of organic ligands. Such level of understanding of mineral dissolution mechanisms, in turn, will be highly beneficial for design of selective, cost- and energy effective extraction schemes for those minerals.

2.2. Minerals alteration in soil environment for agricultural application

The above sections demonstrate that a significant body of knowledge about far from equilibrium dissolution of K-bearing silicates is available. However, the mechanism of mineral dissolution in natural conditions is complex, one of the outstanding factors being the soil environment itself. It is generally proposed that the rates measured in the field are significantly slower than those obtained in the laboratory, though hardly predictable[110,111,115]. Modern geochemical kinetic modelling allows to predict weathering rates in different soils and climates, but requires input parameters such as pH and bulk density of soil, contact surface area, average rate of nutrient uptake by plants, and fluctuations of moisture content[112,113]. Moreover, laboratory experiments typically do not reproduce the actual fluid paths in the soil as well as the soil chemistry. Taking into account the biota dynamics and symbiosis effect makes the situation even more complicated. Though plants, microbes, fungi and bacteria are known to be involved in the natural alteration of minerals[114], limited data are available on the actual mechanisms of K-bearing silicate minerals dissolution coupled with plant growth and harvesting[115,116,117].

Kinetic models that integrate the variability of temperature and fluid composition; the changes in textural and chemical properties of mineral surface; the partial surface wetting, and the role of biota are still missing. Such modelling calls for further multidisciplinary studies, which will allow to predict the rates of natural mineral alteration with a better accuracy. From the perspective of green fertilization, detailed understanding of the inorganic and organic (bio) chemistry involved in minerals dissolution is needed to evaluate the chances of success of as-ground K-bearing silicates for fertilizing application ("stone-meal" approach). This knowledge will help to define the minerals candidates with the most appropriate geological histories that perform most efficiently for a given soil composition and crop culture, allowing their direct use for agricultural application. The use of as-ground material offers the most sustainable alternative to existing inorganic fertilizers, since it requires the minimal amount of chemical processing and mechanical energy only. However, as discussed above, the dissolution rate and the availability of the K from such minerals may not suffice for all soils and agronomical practices. Also, this approach is not possible for Al extraction, suggesting that chemical processing is critical to transform K-feldspar resources into reserves.

3. Hydrothermal processing of K-bearing silicates

From the perspective of chemical processing of K-bearing silicates, for fertilizers or alumina production, the processes proposed to date favour the use of strong acids or basis and temperature, i.e. *hydrothermal* processes. The environmental impact of those reagents has been established[118,119], and their by-product status makes them affordable. Though alternative reagents may become available, as suggested in section 2, it is within this paradigm that most processes have been developed as reviewed below.

3.1 Classification and scope of processing schemes

The most recent review of hydrothermal methods has been published in 1998[24], adopting an approach similar to the one published 86 years earlier[23]. Both are comprehensive in terms of factual chemical engineering procedures, but do not highlight the chemical mechanism and the structure-property relations that constitute their basis. As mentioned in Section 2, the covalent nature of aluminosilicate anions constituting the framework of K-bearing tectosilicates ultimately implies that their water-mediated reactions at ambient temperatures and pressure are often kinetically controlled, i.e. the intrinsic reaction rates are slower than the transport of the reactants/products. Most of the hydrothermal techniques have therefore been designed to accelerate the rate of hydrolytic degradation of the aluminosilicate anionic framework.

The proposed hydrothermal processes can be separated in the following categories: **(i)** techniques aiming at complete mineral decomposition i.e. dissolution followed by recovery of aluminium and potassium as salts from aqueous solution[24,120,121,122,123] and **(ii)** mineral alteration by aqueous solutions of extreme pH, where the products (typically, a mixture of the parent mineral and newly formed phases) are subjected to subsequent extraction of potassium by leaching or ion-exchange[124, 125, 126.]

The processes in category (i) aim to fully dissolve the mineral in strong inorganic acids or bases, and seek the separation of the silica ions with subsequent recovery of aluminium and potassium in the form of crystalline chlorides[121], nitrates[127], and sulfates[123]. In order to reach completion and acceptable rate for industrialization, elevated temperature and pressure are chosen to accelerate the reaction kinetics, along with an aggressive agitation and large amount of mineral acids or alkaline/alkaline earth hydroxides (typically, $Ca(OH)_2$), as well as about around 10-times the amount of water needed for stoichiometric extraction.

The complete extraction of crystalline salts of K and Al from K-bearing aluminosilicates requires a separation step, an energy intensive process seeking to isolate silica from the reacting system. The most common method is a drastic change of the pH implying a large consumption of acids and bases. The next step is a physical separation of colloidal silica from the solution, again an energy and capital-intensive unit operation. This separation leaves behind highly alkaline or acidic residues, which have to be handled as a liquid chemical waste. If crystallization of KCl, KNO_3, K_2SO_4, etc. is involved, water has to be evaporated requiring a significant energy input. From a sustainability standpoint, such complete extraction process has very similar features to the Bayer process used for aluminium extraction from bauxite. Such extraction concept unavoidably causes a large amount of liquid and solid waste if aluminosilicate minerals are used as a raw material, which contradicts with a key principle of green chemistry and engineering, which aims to "*maximize the incorporation of all materials used in the process into the products, and prevent creation of wastes rather than treat or clean up waste after it has been created*"[128]. In addition, complete disintegration is very capital, energetical and chemical intensive in order to be conducted in an environmentally acceptable manner[129]. The only, somewhat unique, example of industrial application of such full extraction process for feldspathoids is with nepheline, to produce alumina for aluminium production. It is currently in operation in a small number of countries from the former Soviet Union[130,131.] Historically, the lack of suitable bauxite in Russia and the occurrence of high grade nepheline ores along with the request of soviet authorities for domestic production of this metal help to contextualize the origin of such complex hydrothermal extraction scheme. The issue of siliceous wastes from such process is unavoidable, and was partially solved by the obligation of the cement industry to utilize them for the manufacturing of “nepheline cement”. The wastes of nepheline refining are indeed enriched in dicalcium silicate (Ca_2SiO_4, belite) - an industrial mineral contained in Portland cement and responsible for the development of late strength of concrete. Being capable of hydrolytic hardening, such belite-rich waste was successfully applied in construction. Another potential solution to the problem of waste handling during alumina recovery from nepheline is the combined processing of nepheline to produce soda, potash, Portland cement and alumina[132,133]. Complete recovery of a minor component from a mineral is challenging due to the need for excessive amounts of synthetic chemicals, water, along with the inherent amount of waste generated by separation steps. Although it is possible to envision a completely “environmentally neutral” process for the separation of $KAlSi_3O_8$ into alumina, silica and a salt of K, the encumbered capital, operating and energy costs have to date prevented its industrial-scale development.

The processes of category (ii) rely on dissolution/re-precipitation promoted by relatively low amounts of alkali/alkali earth hydroxides. These processing schemes typically do not allow the transport of the dissolved products and lead to in-situ re-precipitation – conditions commonly achieved in batch, semi-batch, and sometimes, continuous reactors without agitation[124,134]. For such high over-saturation conditions, the space constraint leads to the precipitation of poorly crystallized products, or a mixture of crystalline and semi-crystalline precipitates. The discrimination between the steps of hydrothermal dissolution and ions precipitation is however very challenging conceptually and experimentally[135]. As a practical example, another commercially important group of materials produced using a similar process are synthetic zeolites. For this group of material, the fundamental understanding of hydrothermal crystallization/condensation is still in its developing stage, despite being industrially conducted since 1950. Altogether, there is still a lack of information about the intermediate phases formed in solution and in the vicinity of the surface[136]. The interest for these processes lies in their ability to generate only solid products and by-products, which are easier to handle, transform or stockpile than liquids. Chemical identity and physical state of by-products are in part linked to the degree of conversion of the original mineral, dictated by the technology suggested by the inventors. A shorter time, less aggressive conditions and a lower temperature and pressure clearly favour the economics and enhance the sustainability of the process, but also tend to lower the degree of conversion.

None of the processes from category (ii) have yet been successful applied for large-scale potassium extraction from K-bearing tectosilicates. To evaluate the viability of such processes, and allow their relevance at large-scale, the performances of the precipitated products for a given application must be optimized. From that standpoint, the proposed processes have rarely been designed and conducted with a thorough characterization of the intermediate products formed at each steps, so that it is currently not possible to predict their performance, for example from the perspective of their agricultural application. From the green chemistry standpoint, processes from category (ii) may be more suitable processing options, because they do not require separation, liquid waste handling, and significant water recovery. In other words, hydrothermally driven mineral alteration aimed at increase in availability of ions of interest (e.g., potassium) meet the “atom economy principle”, which declares that “*synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product*” [124]. The limitations in our knowledge described in section 2 for the fundamental chemical mechanisms, as well as the difficulty of in-situ monitoring for hydrothermal reactions, are calling for more thorough and multi-disciplinary research. The next section represents a brief summary of fundamentals relevant to hydrothermal alteration of aluminosilicate minerals.

3.2. Hydrothermal dissolution – re-precipitation of K-bearing silicates in aqueous fluids

Hydrothermal dissolution of aluminosilicate minerals and glasses involves the same chemical events as the ones described for dissolution at ambient conditions, discussed in section 2[137,138,139]. The water-mediation model offers an acceptable framework for discussion, whether or not a visible liquid phase has been isolated in the proposed hydrothermal methods[135]. Accordingly, the key chemical steps are the breaking of T-O-T bonds (hydrolysis) and the formation of new bonds (condensation), both mediated by water and promoted by H^+ or strong nucleophiles (e.g. OH^- or F^-). Temperature and pressure are typically higher than 100°C and 1bar respectively, so that the dielectric constant of water and the viscosity decreases, improving the solvation power and the mobility of the water molecules[62] (section 2.1).

For a fixed pH, the chemistry of the anionic species resulting from the mineral dissolution is determined by their electronegativity, charge and the coordination number of the oxide-forming element[62,78]. At high saturation states and pH above 7 - conditions commonly proposed for the processing methods of category (ii)[23,24,124,125,126] - metastable precipitates form and re-dissolve slowly. The speciation of silica and alumina in such conditions is very sensitive to the time-temperature history, the fluid composition or the presence of a mineral surface[78]. Solutions oversaturated with respect to silica at high pH, for example, contain monomeric silica anions $SiO_x(OH)_{4-x}^{x-}$ coexisting with molecular $Si(OH)_4$ and polynuclear (polymeric) species. The increase in pH promotes deprotonation and depolymerization of aqueous silica, while increasing ionic strength may cause loss of stability and ultimate precipitation in amorphous state[78]. The structure of such precipitate is determined by the initial size distribution of the silica anions, with more compact silica gel inherited from a larger amount of monomers in solutions obtained at high pH[61].

Chemistry of oxides of IIIB group such as aluminium (ionic radius 0.5 Å) differs from that of silicon (ionic radius 0.42 Å) due to the lower electronegativity of the former and its ability to form complexes of coordination number greater than 4. As far as Al^{3+} aqueous speciation, its coordination number with water is commonly 6, and the unhydrolized cation $[Al(OH_2)_6]^{3+}$ exists below pH=3. With increasing pH, Al^{3+} forms polynuclear ions, e.g., $[Al_3(OH)_4(OH_2)_9]^{5+}$ and the Al^{13}- ion[78]. Aluminium ions, in turn, can pre-combine and co-polymerize with siliceous anions, with a high sensitivity on variations in temperature, composition/pH, or rates of precipitation. Aside from those factors, a catalytic role of F^- deserves special attention. In aqueous solutions, fluoride ion is a nucleophilic agent as strong as OH^- and tends to coordinate directly with Al and Si, weakening the Si-O-Al bridges, and leading to the formation of hydrophobic Si-O-Si bridges. The presence of even minor F^- impurities can therefore increase both dissolution and precipitation rates in hydrothermal reactor, and influence the final state of the dissolution products[77,140]. Besides amorphous products, crystallization of crystalline silicate phases can also be observed in hydrothermal reactors. For example, hydrothermal treatment of feldspars with lime ($Ca(OH)_2$) typically results in the formation of tobermorites[141,142] a calcium silicate hydrates with chemical formula $Ca_5Si_6O_{17}(OH)_2\bullet 5H_2O$ or $Ca_4Si_6O_{15}(OH)_2\bullet 5H_2O$. Tobermorites are characterized by their different basal spacing and can adopt various structures depending on the process conditions[143]. Although crystallization of the new phases occurs in the direct vicinity of the mineral, epitaxial growth is not guaranteed[144].

Perspectives

Despite a substantial scientific background, many technological attempts, and geopolitical motivation, the industrial usage of primary K-bearing rock forming minerals in global materials extraction is scarce. Dissolution kinetics makes the low-temperature natural extraction from these minerals unlikely to provide access to K and Al at a rate of industrial relevance, as depicted in section 2. Therefore chemical processes have to be envisioned, if possible adopting green chemistry principles. As far as traditional extraction techniques based on full extraction (category (i)), their considerable energy cost and the need for handling the corresponding by-products has prevented their industrialization in the free global market, and are challenged by green chemistry concept. With such realities in mind, only synergetic approaches seem viable, i.e., processes from category (ii), where "synergy" implies avoiding wastes generation by incorporating a maximum of beneficial components and using local energy sources. Building up on the remarkable advances of the zeolites industry, a precise control in the hydrothermal dissolution-precipitation treatment of K-bearing feldspars and feldspathoids may provide the desired structural arrangement of the precipitated products with a microstructure and a phase composition suitable to obtain a controlled rate of potassium release and/or enhanced weathering rate during agricultural application.

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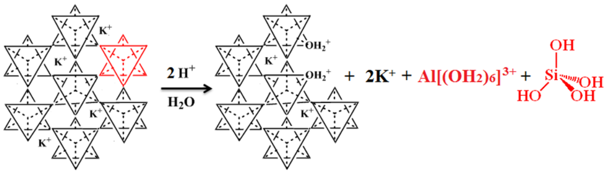

Potassium-bearing framework aluminosilicates are earth-abundant and globally available raw materials with a high content K_2O and Al_2O_3, and offer a possible alternative source of potassium or aluminium for the developing countries. The aqueous alteration of these minerals has traditionally been proposed as one processing route. The underlying chemistry and processes are discussed in this work, in the framework of green chemistry principles.