SILICON ALKOXIDES AND LUNAR DEVELOPMENT. S.L. Gillett, 2395 Wildflower Dr., Washoe Valley, NV 89704; gillett@alumni.caltech.edu.

Introduction: Lunar regolith, being merely crushed rock, is an unpromising feedstock for industrial processes despite containing a wide variety of potentially useful elements (e.g., O, Si, Mg, Al, plus traces of H from solar-wind implantation.) The unreactivity of the common silicates that make up ordinary rock makes element separation very difficult. For such reasons similar materials are not used as mining feedstocks on Earth.

Using lunar regolith, however, is widely thought to be necessary for establishing a lunar infrastructure, and a number of schemes have been proposed. Most are directed toward oxygen extraction, but some address metals or Si extraction as well. All have serious disadvantages. Electrolysis of a silicate melt ("magma electrolysis")[1] and direct pyrolysis[2] have been impractical because of the extreme temperatures involved. Low-temperature processes based on hydrogen fluoride (HF) or elemental fluorine (F_2) avoid this problem[3], but not only do these reagents need to be imported, they are both highly toxic and exceedingly corrosive. Moreover, the resulting highly stable fluorides and fluorosilicates are not useful products, and are difficult to recycle back into HF or F_2.

Surprisingly, though, a number of organic reagents are capable of dissolving silicates [4], so that approaches based on such reagents promise to combine the low temperatures of F-based processing with considerably lower toxicity. In many cases the reaction products are also themselves immediately useful.

Si Alkoxides: Among the most interesting organic-based processes are those that yield silicon alkoxides (organic silicates), of which the simplest have the general formula $Si(OR)_4$, where R is an alkyl group. Certain of these compounds have relatively low toxicity, in particular tetraethoxysilane (TEOS), $Si(OC_2H_5)_4$. Si alkoxides are volatile liquids (boiling points ~40°C) that would be relatively easy to separate (e.g., by distillation) from the reaction mixture and that would also be easy to handle. Unlike the fluorides and fluorosilicates that result from F-based processing, silicon alkoxides are also immediately useful materials, because they are the basis of the "sol-gel" synthesis of ceramics, which has attracted an enormous amount of attention over the last few decades[5]. Reaction with water causes formation of Si-O-Si bonds (disiloxy linkages) between adjacent molecules, with the release of 2 molecules of alcohol (ROH):

$$2\ Si\text{-}OR + H_2O \Longrightarrow Si - O - Si + 2\ ROH$$

As reaction proceeds, a 3D network of disiloxy links develops to form a *gel*; this can be sintered at modest temperature to drive off the remaining water and alcohol to yield a glass.

Furthermore, the alcohols and water given off during the curing of an alkoxide gel could be easily and automatically recycled as they are compatible with the life-support system. Due to the extreme dearth of C and H_2O on the Moon, of course, recycling of reagents is critical as nearly all will need to be imported. Also, as little imported material as possible should be permanently consumed in construction. Silicon alkoxides also are advantageous here, because only Si and O are permanently consumed in making the gel; the water and alcohol, which of course must be imported, are given off automatically during reaction where they can be recycled.

The use of silicon alkoxides *alone* to generate ceramics for structural use would obviously requires a very large lunar-based manufacturing facility, which is unrealistic in the near term. Instead, methods should be investigated of minimizing the quantities of alkoxides required by using them as glues or binders. One obvious approach is as follows. Dampened regolith could be mixed into TEOS to make a slurry that would cure into a solid composite. The trace of added water will not only trigger gel formation, but will form hydroxyl (-OH) groups on the regolith silicate grains, which will then react with the TEOS to form strong disiloxy links. The result would be something like a sintered brick but obtained at far lower temperature. Most water and ethanol could then be recovered and recycled.

It is also possible that TEOS could be reduced to elemental silicon, perhaps by reactions such as:

$$Si(OC_2H_5)_4 + 2\ H_2 \Longrightarrow Si + 4\ C_2H_5OH.$$

This could be a way of producing extremely pure Si for semiconductor use. TEOS finds use at present in chemical vapor deposition of silica films [6], but whether it can be employed to deposit elemental Si is unclear.

As described below, too, the process for extracting Si alkoxides from natural silicate-dominated mixtures such as regolith will also leave a residue enhanced in potentially valuable elements.

Formation of Si alkoxides from regolith: Silicates containing isolated anionic groups, most simply the orthosilicate anion, SiO_4^{-4}, are disrupted by strong mineral acids (they "gelatinize"). Such silicates, olivine for example, can react in acidified alcohols to form alkoxides directly, e.g.:

$$Mg_2SiO_4 + 4\ H^+ + 4\ C_2H_5OH \Longrightarrow Mg^{++} + Si(OC_2H_5)_4 + 4\ H_2O\ [7].$$

The reaction is driven to the right by removing the water as fast as it's formed. Indeed, the "scarce water" conditions on the Moon should make water removal easier; this is one case in which the Moon's utter waterlessness may prove useful. The volatility of silicon alkoxides also should make them easy to distill off and purify under lunar conditions.

Olivine is locally common on the Moon, but most lunar minerals, as well as impact glasses, are insoluble in mineral acids because they are highly polymerized, (i.e., highly crosslinked with disiloxy bonds). Acid (i.e., H^+ ions) does not attack the Si-O-Si bond. However, polymerized *alumino*silicates, which contain aluminum as part of the polymeric framework, are vulnerable to acid attack at the Al-O-Si linkages[8]. In particular, anorthitic plagioclase (90%-100% anorthite ($CaAl_2Si_2O_8$) content) is known to gelatinize under attack by acid, and such calcium-rich feldspar is common in the lunar highlands. Hence it probably will also react to form alkoxides in acidified alcohol solution.

In addition, the other cations (Mg, Fe, Al, Ti) in these silicates will not form alkoxides under these circumstances but will be left behind as metal salts. Thus alkoxide formation seems promising as a way to separate Si from other oxides, from Al in particular.

Regolith, of course, also differs from place to place as it largely reflects the underlying rock composition; most strikingly, of course, in the contrast of the highlands vs. the maria. Thus, the different reactivities of the components of the regolith may well provide a convenient way of separating them.

The residue of unreacted material may also prove useful. Not only will it consist of some unreacted silicates, but it will be enriched in non-silicate minerals such as oxides, phosphates, and sulfides. Any of these, if sufficiently concentrated, could also be useful resources.

References: [1] e.g., Agosto W. N. (1983) *Adv. Astronaut. Sci. 53*, 275. [2] e.g., Haskin L. A. et al. (1992) *The Second Conference on Lunar Bases and Space Activities of the 21st Century*; Colson R. O. & Haskin L. A. (1993) *Resources of Near-Earth Space*, pp. 109-127, University of AZ Press, Tucson. [3] e.g., Waldron R. D. (1985) *Proc. Seventh Princeton-/AIAA/SSS Conf.*, pp. 132-149, AIAA; Agosto, W. N. (1992) *Engineering, Construction, and Operations in Space III, Vol. 1*, p. 678.; Seboldt W. et al., (1993) *Resources of Near-Earth Space*, pp. 129-147, Univ. AZ Press, Tucson. [4] review in Gillett S. L. (2001) *Return to the Moon II: Proceedings of the 2000 Lunar Development Conference*, pp. 240-6. [5] e.g., Brinker C.J. & Scherer, G.W. (1990) *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing* Academic; Pierre, A. C. (1998) *Introduction to Sol-Gel Processing* Kluwer. [6] e.g., Jones A. C. & Hitchman M.L., eds. (2009) *Chemical Vapour Deposition: Precursors, Processes and Applications*, RSC. [7] Goodwin G.B. & Kenney M.E.; *ACS Symp. Series 360*, 1988, pp. 238-248; US patent 4,824,985, 1989; *Adv. Chem. 224*, 1990, pp. 251-263; *Inorg. Chem. 29*, 1216, 1990. [8] Murata K. J. (1943) *Am. Mineral. 28*, 545-562