

SESSION IV

SODIUM SILICATE AS A VERSATILE STRUCTURAL MATERIAL

Herbert I. Hoffman, Senior Research Engineer

Department of Mechanical Sciences
Southwest Research Institute, San Antonio, Texas

INTRODUCTION

The family of soluble silicates includes the well-known, inexpensive sodium silicate, commonly called water glass. Soluble silicates are produced by reacting silica sand with appropriate alkalies, resulting in opalescent, viscous liquids in solution with water. Partly dehydrated, they are also available in various powder forms. Rapid boiling of the solutions or of the hydrated solids causes an intumescence or foaming, which is the characteristic that is of special interest in this paper. As an industrial chemical selling for under 3 cents per lb in bulk, the soluble silicates are used directly in adhesives, detergents, specialized paints and fire retardants. Beginning with an 1883 patent, there is an evolution of industrial applications based upon using the foamed material for its insulation value, both thermally and acoustically.

While using sodium silicate solution as a high temperature adhesive, the foaming resulting from thermal exposure with high temperature applications became of interest. Foamed samples were then prepared by simple boiling and by more complex methods of heat input. Sections of two laboratory-produced foams are shown in Figure 1. The larger disc was foamed under reduced pressure in a bell jar; the significance of ambient pressure versus heating rate is of major interest. It became evident that 10 lb per cu ft foams of structural quality could be produced for approximately 9 cents per lb, contrasted with a minimum of about 55 cents per lb for plastic foams with similar physical properties (1).

Aside from unusual performance possibilities, the potential cost savings are enough to encourage interest in applications where mass production of expendable components is desirable. For example, quickly erected insulated shelters and inexpensive, expendable air drop cushion packages are two possibilities of special interest. In space applications, other qualities of sodium silicate offer advantages over present chemical rigidizing and foaming systems. Furthermore, it offers an excellent potential for an

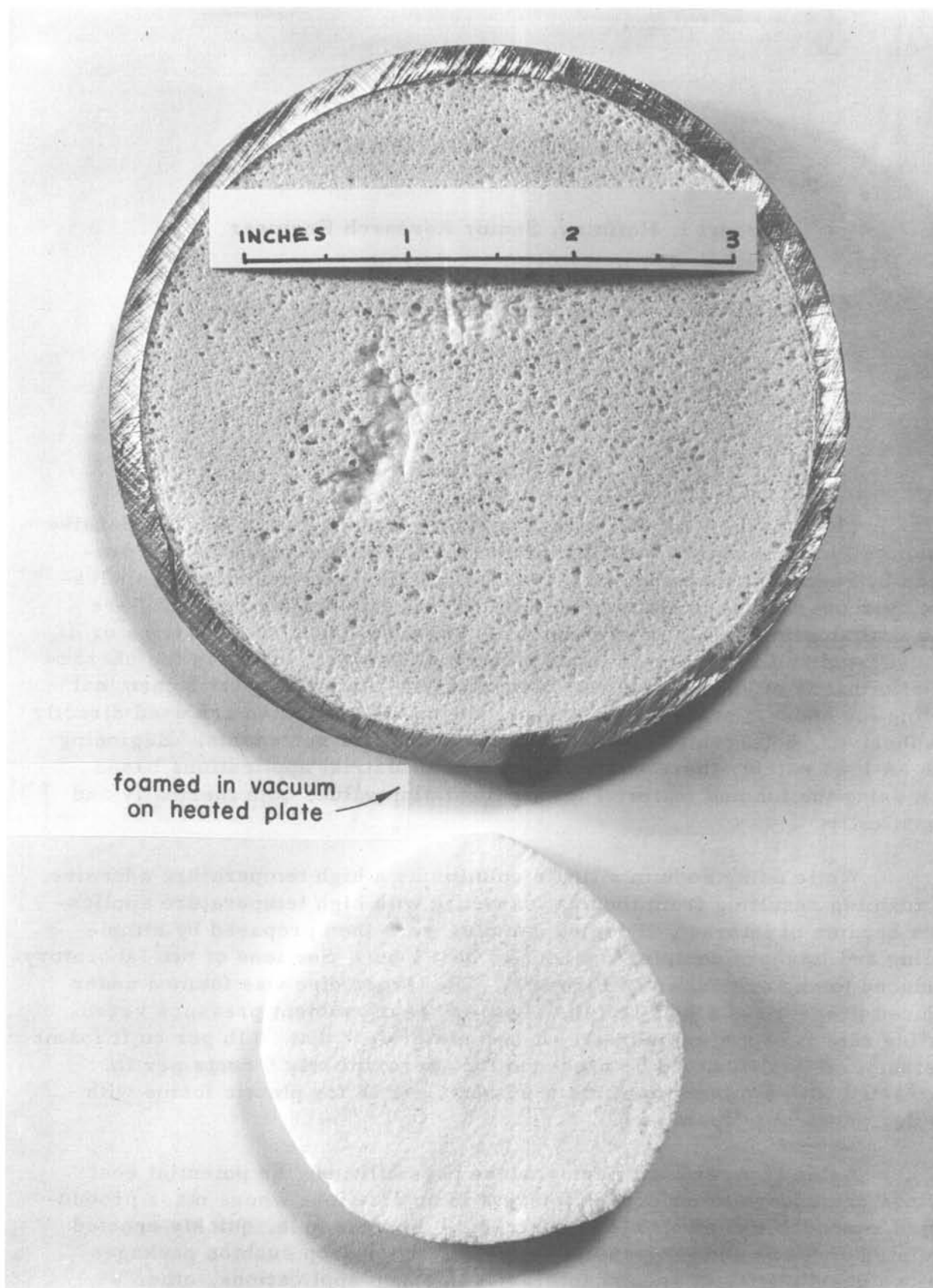


FIGURE I. RIGID SODIUM SILICATE FOAM

inorganic, thermal insulation and heat sink which could be shaped in space.

TECHNICAL BACKGROUND

Sodium silicate is widely used in industry as an agent to control the physical properties of solutions. It is used as a wetting agent, as a heavy-duty cleaning compound, and as an emulsifying agent. Its properties as a binder, sealer, and adhesive are among its major commercial attributes. In soil stabilization, the reaction between sodium silicate and clay soils has become a technology of its own. Sodium and potassium silicate compositions are very well accepted as binders in the manufacture of heat resistant paint and coatings. Some coatings with silicates will perform well at temperatures approaching the melting points of the protected metal parts (2). Fire retardance continues to be one of the major fields for soluble silicates. Their bonding strength and thermal resistance are useful in the manufacture of refractory materials, including blocks and cement. Figure 2 tabulates the chemical compositions and physical properties of soluble silicates.

Perusing through the complex chemistry of silicates, a designer is sharply reminded that the exact composition of the material can be identified only from the crystalline form. The composition of sodium silicate is readily modified by common contaminants and additives; fortunately, this has not been a problem in foaming experiments.

In developing design concepts, it should be noted that the boiling point of silicate solutions is slightly above that of water at normal pressure, while a typical freezing point is approximately 2° below that of water. Dense solutions of sodium silicate suffer little from freeze separation which might be anticipated due to exposure in the vacuum of space.

Densities of commercially available sodium silicate solutions vary from 11 to over 14 lb per gallon. In solid forms, it is available in sizes from lumps through fine powders. Their densities range from approximately 55 to about 88 lb per cubic foot, covering hydrous and anhydrous forms.

The discussions in this paper are based upon experiments with sodium silicate, which is the most common and least expensive of that family of soluble silicates. Potassium silicate, also commonly available, is somewhat more expensive and has not been considered in the preliminary experiments.

Physical Forms and Their Uses

As suggested by the traditional applications mentioned previously, sodium silicate has many forms. Figure 3 illustrates some of the "solid" forms which can be generated by heat and vacuum. The two paths indicate

HYDRATED SODIUM SILICATES

$\text{Na}_2\text{O} : \text{X} \cdot \text{SiO}_2 : \text{H}_2\text{O}$ -----indicates oxide proportions in typical water glass
ratio 2.5 to 3.5 of interest $\left\{ \begin{array}{l} \text{various \%} \end{array} \right.$

Example: $3 \text{Na}_2\text{O} \cdot 13 \text{SiO}_2 \cdot 11 \text{H}_2\text{O}$; specific gravity 1.13

ANHYDROUS SODIUM SILICATES

- $\text{Na}_2\text{O} \cdot \text{SiO}_2$ - sodium metasilicate: melting point 1089°C
- $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ - sodium disilicate: m.p. of various crystal forms: 678° , 707° , 874°C
- $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2$ - polysilicate: m.p. 820°C . When dissolved in 15% of H_2O and heat foamed, results in 30 to 100 expansion; thermal conductivity about .029 Btu/hr-ft²-deg F.

FIGURE 2. PROPERTIES OF SOLUBLE SILICATES

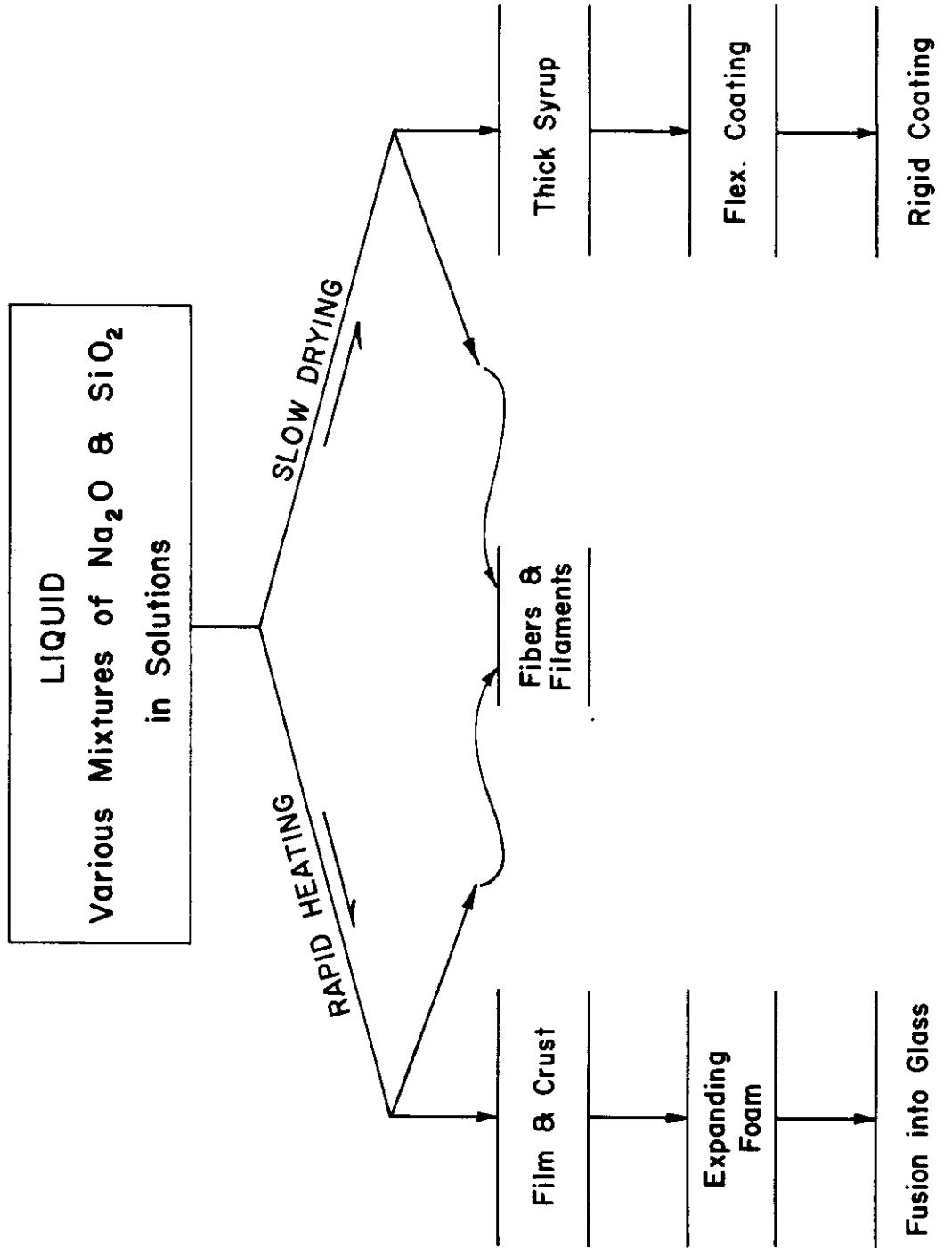


FIGURE 3. FORMS GENERATED BY DEHYDRATION

the successive effects of rapid heating, including exposure to flame, vs. the effects of slow dehydration. Preliminary experiments conducted in a vacuum bell jar indicate that the same forms indicated here can be achieved in vacuum, perhaps with supplemental heat in some cases. This suggests the possible values of self-activation in space. It will be noted that the silicates can be drawn into fibers and filaments which can be solidified by heat or vacuum. This suggests possibilities of building or winding structures in place. Slightly more conventional is the concept that fabric ribbons saturated in liquid sodium silicate could be used for repair or construction in space, resulting in an immediate curing of the coating into a reinforced glass structure capable of foaming under intense heat.

Continuing to follow Figure 3 down the rapid heating approach, it is indicated that rapid heating of the solution will form crusts of glass which in turn will finally generate into a rigid, coarse foam as heating continues. Exposure to still higher temperatures in excess of 600°F at atmospheric pressure, the rigid foam continues to expand into fine, white rigid foam. When this material is further exposed to flame or other extreme heating, the rigid foam enters into the molten state. The slow dehydration path indicated on Figure 3 perhaps is not as immediately thought provoking from a design point of view. However, this process carries the solution through a thickening into the glass state. Under vacuum exposure, it is likely that freezing and drying would continue unless supplemental heat were provided to cause foaming.

The compressive strength of a laboratory sample of foam is illustrated in Figure 4. After initial crushing, the load for continued crushing leveled off at about 40 and 50 psi for the two relatively slow loading rates. Impact loads would run higher. Additives would probably increase those values significantly.

Application Problems

Conduction heating and gas foaming methods of generating silicate foams and procedures for foaming in place are described in the literature. The generation of silicate foams by boiling or rapidly heating the liquid solution has been used to manufacture refractory blocks and insulating boards; however, this heating method has not been appropriate for generating foam in place except where the walls of the cavity to be foam-filled can withstand the required heat of conversion. Some of the documented uses of silicate foams involved prefoaming pellets of the material and, in turn, bonding those together in place with resorting to further heating.

One question faced by a designer is the solubility of the rigid foamed silicates. Fortunately, the solubility of sodium silicate foam in boiling water can be brought to a negligible value either by exposure of the foam to

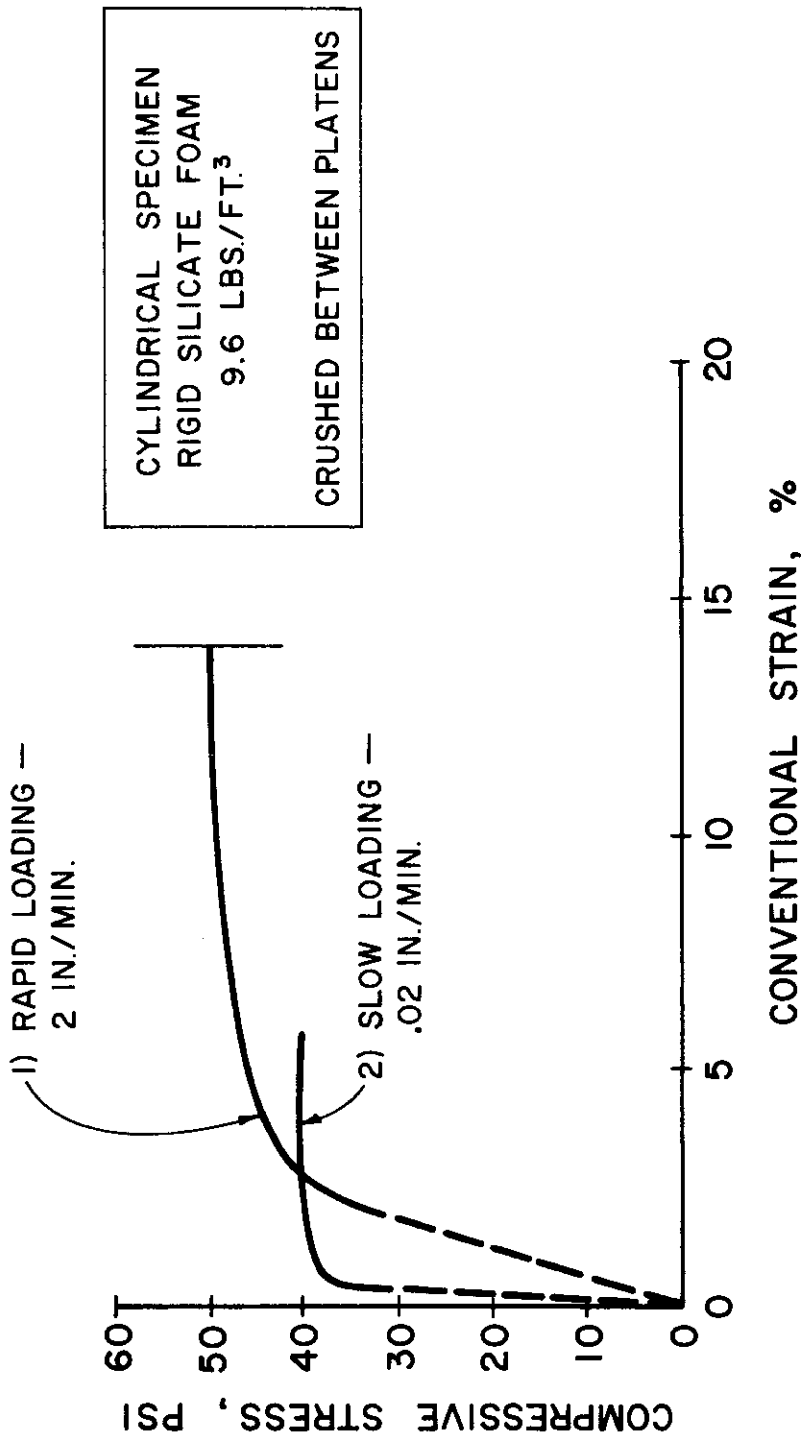


FIGURE 4. CRUSHING STRENGTH OF RIGID FOAM

an acid gas or by proper composition of the solution from which the foam is made.

It is with this background of the chemistry, the mechanics, and economics of sodium silicate that the demands of expanding and rigidizing structures for space applications and for limited war applications must be considered. Methods of heating (beyond conventional conduction) must be considered. For expandable structures which might require flexible skins of plastic or fabrics, it might be necessary to place the foams or to rigidize these structures without endangering the skins by extreme heating. At the same time, space applications offer an obvious and unique possibility for rigidizing; the hard vacuum can promote dehydration and freeze drying of the material. Where rigidizing alone is of interest, a rigid crust resulting from vacuum drying may be sufficient. The generation of rigid silicate foam in space would require heat to supplement the dehydration effect of vacuum.

Having set the stage, we now enter upon another portion of this subject.

CHOICES IN PROCEDURE

Mechanical Features

Thus far, we have generalized on the physical forms which might be useful in expanding and rigidizing of collapsible structures. Summarizing, we can choose 1) the relatively simple step of rigidizing a flexible matrix by vacuum and/or heat dehydration of its coating, or 2) the more complex applications going beyond the rigid coating into expansion of rigid foam. In evolving conceptual designs, it is necessary to assume not only the properties of the expandable and/or rigidizing medium, but the means for accomplishing that change of properties.

Conversion Methods

There is always the choice of using expansion methods based on gas generation, which is inherent in many foaming processes. Gas generation due to chemical reaction, instead of vapor or steam generation from rapid boiling, poses a different set of problems, but should be considered. The fact that a rigid foam can be generated from an inexpensive solution by simply boiling the material, offers advantages for many terrestrial applications where economics and low shipping volumes are important.

To face the numerous expandable structure problems which have been evidenced by our discussion today, we are forced to consider more than the simple boiling or conduction heating of the solution to generate rigid coatings and foams. For example, it is to be considered that for some

space applications, such as a solar collector to be rigidized, it may prove reasonable to pigment the material so that radiated energy absorbed by the structure will be sufficient to harden it quickly.

For generating foam samples for laboratory study, excellent results have been obtained using a radar oven or microwave oven to produce internal heating and subsequent boiling and foaming of sodium silicate solutions. By microwave, samples have been foamed inside Plexiglas shells and in Mylar bags. Microwave or radar heating suggests a possible tie-in between this method of heat application and the communication microwave systems and radar which might be available at a site where foaming is required.

Other foams were expanded from solution poured over molten lead for a heat source.

Electrolytic heating of the sodium silicate solution appears to be an interesting, practical way to achieve foaming. To develop a uniform structure, it would seem reasonable to submerge a series of alternate cathodes and anodes in the solution which, in turn, would be confined in a hollow chamber or cavity which is to be foam-filled. Input of electrical energy through the electrodes would cause resistance heating and result in a foaming of the silicate. A similar approach would be the direct use of resistance wires in a solution. Another class of heating and foaming method is the use of pyrotechnic materials mixed with or laminated to the sodium silicate to be foamed. It is conceived that mixtures such as thermites, including magnesium powder, would burn throughout the solution, causing enough heating to result in a rigid foam. It is likely, of course, that such a process would generate sufficient combustion gases that the gases would have a major effect on the foam structure. Chemically similar would be the common additives of an acid plus a metal in order to generate heat and gas, causing foaming of the material. The electrolytic and pyrotechnic methods have not been attempted on this project.

Flexible Packaging

Packaging films are available which are flexible enough at low temperatures for space applications and still would withstand upper temperatures which would be involved in foaming of sodium silicate solutions. Many of the applications for rigidizing in space with sodium silicate would involve distributing a quantity of the solution between plastic films so that the solution is sealed and protected from the vacuum dehydration which otherwise would occur in space. A flattened storage pouch could be prefolded and would later serve as the skin of an expanded structure.

APPLICATIONS

Limited War Requirements

The perennial problem of air drop cushioning seems to be a natural area in which to consider inexpensive, rigid foams of silicates. Figure 5 suggests collapsed containers, filled with hydrated silicate, to be expanded into rigid, energy-absorbing foam. This can be accomplished in a foaming oven. The foam may be cast monolithically within the cushions, or the container may be filled with pellets or chunks of foam. Where salvage of a flexible cushion or collapsed container is reasonable, the foam may be removed by water or by steam, or by simple mechanical crushing and shaking in the event that insoluble foam has been used. Thus, the cushion containers may be reused when convenient; however, it is believed that the greatest gain might be made by selecting the option in the field of saving shipping cubage through the use of foam generating units at depot level.

A similar operation would use the inexpensive foam for field-expanded shelters. Sealed, compressed, flexible packets containing sodium silicate could be readily transported and stockpiled, together with a fuel-fired oven for expanding them into rigid, molded panels. One advantage of this system is that once panels or building components were expanded and rigidized, they would not require air compressors or blowers in the field to maintain their shape. For economy in shipping weight and volume, it is suggested that a collapsed and packaged component would contain a solid form of hydrated sodium silicate. At a behind-the-lines depot, individual panels or sections could be placed in suitable molds and perhaps heated by conventional military fuels. These panels would thus be heated and expanded into rigid building sections, complete with plastic or coated fabric skins. This has been done for building boards in the past! It could be convenient to use skin materials of camouflaged coloration and to mold contours which would be suitable for camouflaged covering of gun emplacements and vehicles. In other words, artificial boulders or hummocks could be molded in the field for movement by helicopter or other vehicles to the area where concealment is required. An interesting sidelight to this camouflage device is that radar reflectivity, as well as optical appearance, could be tailored into the foam to the extent and pattern desired by the addition of metal powder.

Space Applications

In space system structures, one may consider several types of duties which sodium silicate might serve either as rigid film or as expanded film. For example, a deployed flexible surface can be rigidized by allowing a film of liquid sodium silicate to dehydrate on its surface. This is, of course, similar to the previously demonstrated use of gelatins in rigidizing structures.

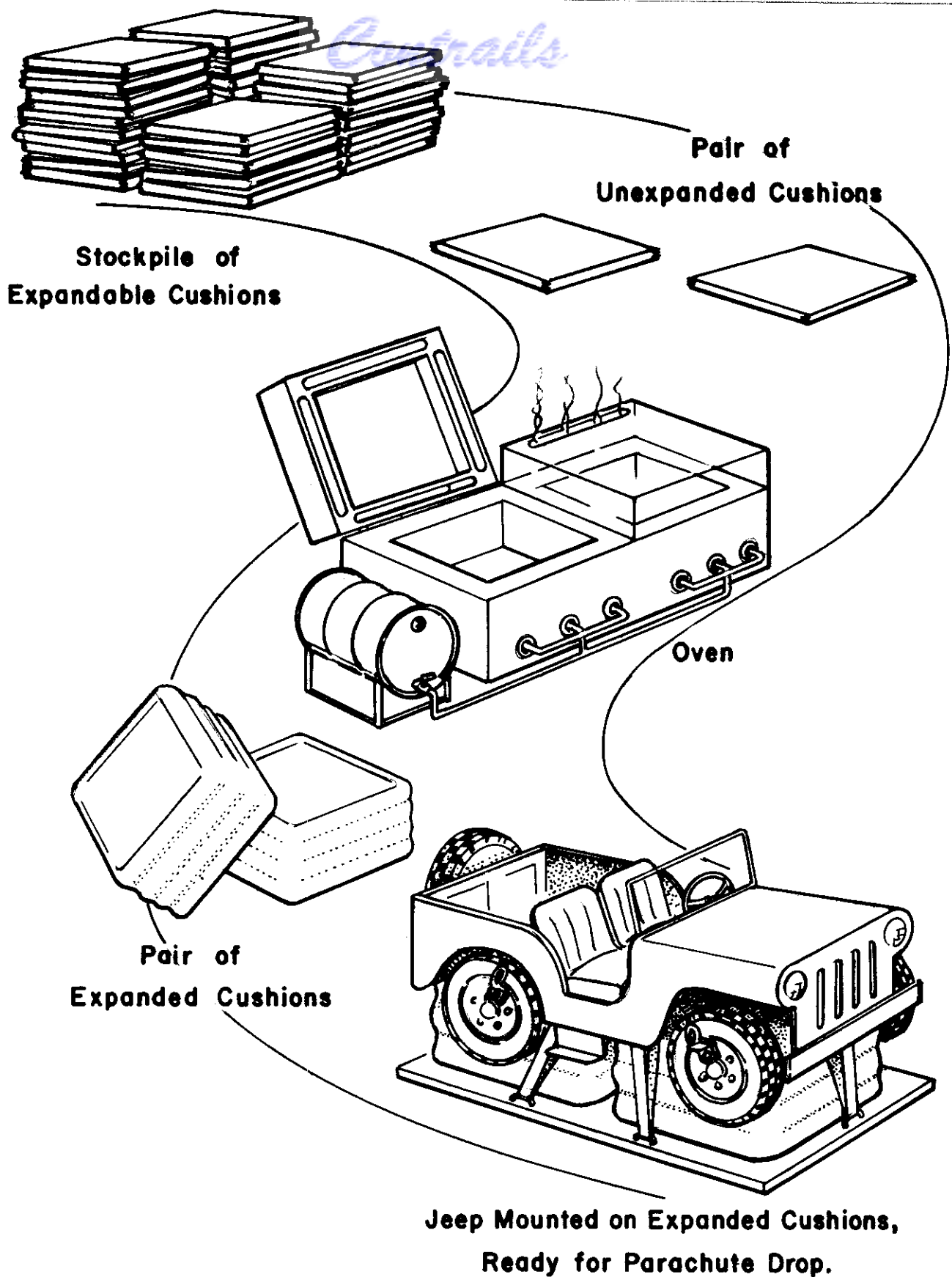


FIGURE 5. SILICATE FOAMING FOR AIR DROP CUSHIONING

Under extreme thermal exposure, the silicate film would expand into a rigid foam.

Now going a step beyond rigidizing, but not necessarily separate from it, are applications based on expanding the sodium silicate from either a viscous solution, a gel, or a hydrated solid into a rigid insulating foam. The relative merits of expanding in space from the liquid or from the solid hydrate could be evaluated only in terms of a specific application. Either form can be foamed within a vented hollow panel or on an exposed surface. The choices of energy to provide heat of vaporization for foaming in space could include radiated thermal energy, packaged electrical energy, and sheet pyrotechnic. In some applications, stored heat from adjacent surfaces would foam the silicate in vacuum. (3, 4)

Expendable Thermal Protection

Sodium and potassium silicates have maintained places as binders in the modern technology of high temperature coatings. A one-time thermal protection is common in many fields, including fire protection in structures. In that field, the intumescence of boric acid, soluble silicates and other hydrates is widely used for its one-time effective heat absorption and insulation. Studies of retention of water and of gelatin for one-time cooling of protected airframe skins have been previously reported.

The properties of soluble silicates indicate that a reinforced layer would serve as a hydrated "plaster" and would, upon exposure to high temperature (for example, during re-entry), foam into an insulating layer while releasing the bound moisture. An example of this application is illustrated in Figure 6.

Many adaptations are plausible, including the combining of an ablative surface with the foaming silicate.

CONCLUSIONS

It would appear that the heat absorption technique of allowing a hydrated coating to calcine can be developed into several useful channels to meet the missions of military and space activities.

Using hydrates which would harden under heat or vacuum exposure would provide a rigidizing technique similar to that accomplished with gels. This is a direct way to capitalize on vacuum-activated rigidization. The next step which may follow in combination with the first is the expansion, in place, of a liquid or solid hydrate into a rigid foam suitable for providing mechanical properties in expandable structures such as those under discussion.

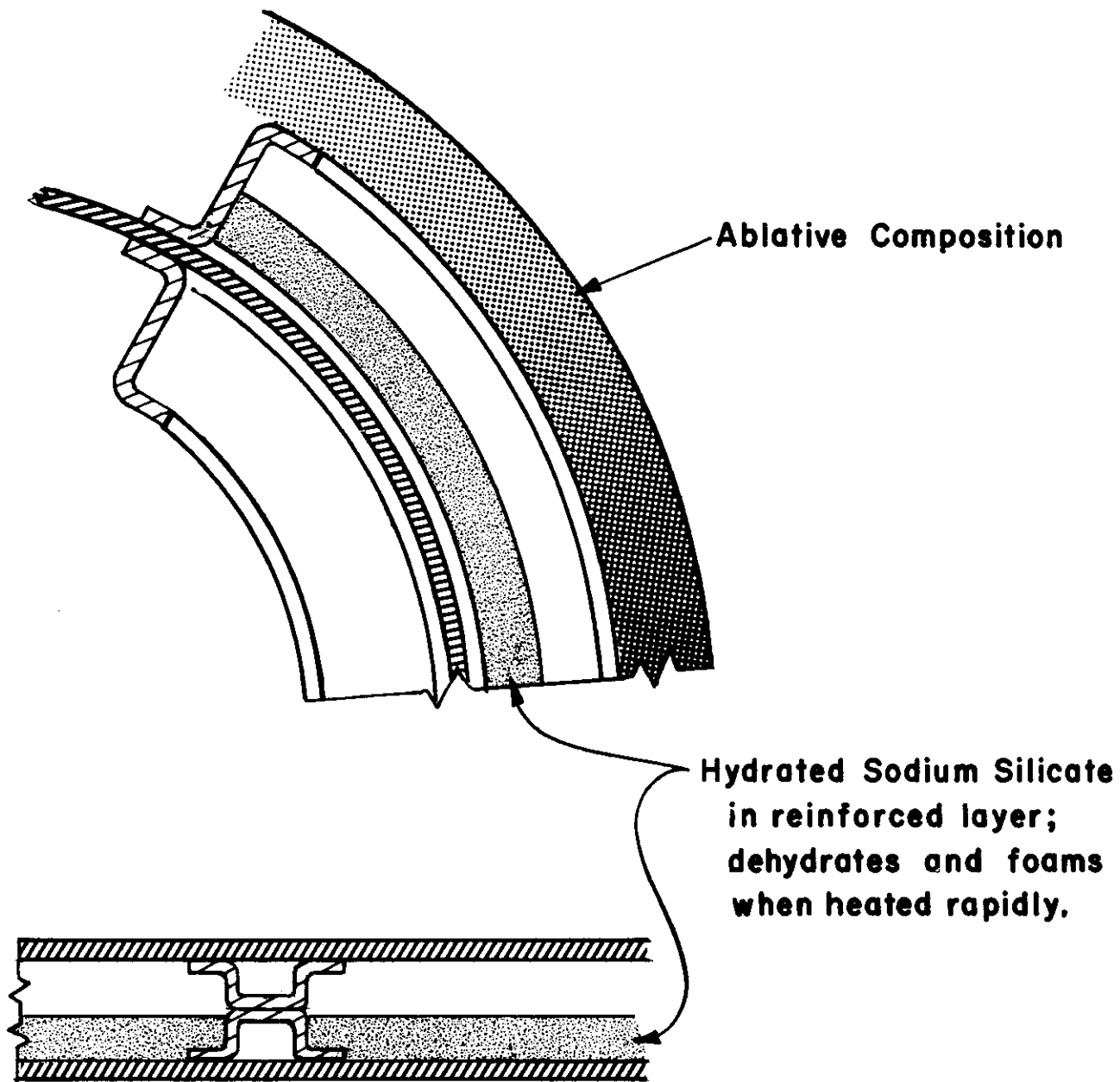


FIGURE 6. THERMAL PROTECTION OF VEHICLE WALL

In the laboratory, foaming expansion ratios range from 3 to 5 times the original liquid volume with good foam properties.

For aerospace applications, rigidizing and/or foaming from mineral hydrates such as sodium silicate probably would offer bonus advantages in thermal properties and long term stabilization compared with organic materials currently studied.

For terrestrial military missions requiring temporary shelters and air drop cushioning, the bonus advantages over reported methods are inherent environmental durability, low cost, and the simplicity of salvaging and later refilling foam-stiffened components in the field.

One of the next tasks in evaluating this material for space applications will be thermal effects in vacuum; this study would be accomplished largely in the SwRI Arc-Image Facility which can provide a sustained flux up to 3,690 Btu/ft²-sec.

LIST OF REFERENCES

1. Ferrigno, T. H., Rigid Plastic Foams, Reinhold Publishing Corp., N. Y., 1963.
2. Vail, James G. and Wills, John H., Soluble Silicates—Their Properties and Their Uses, Vol. 1 and Vol. 2, Reinhold Publishing Corp., N. Y., 1952.
3. NASA Contributions to the Technology of Inorganic Coatings, National Aeronautics and Space Administration, Technology Utilization Division, NASA SP-5014, 1964.
4. Hurwicz, H. and Mascola, R., "Thermal Protection of Satellites With 'Cold Wall' Ablation," Avco Corp.; American Rocket Society, Oct. 9-15, 1961.