65th Porcelain Enamel Institute Technical Forum

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Conference Director

Steve Kilczewski
Assistant Conference Director

William D. Faust
Editor

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Richard Lehman, Rutgers University

Basic Steelmaking
Larry Steele, Mapes and Sprowl Steel

The Relationship Between Contamination and Cleanliness as it Relates to Porcelain Enamel
Mark Godlewski, Henkel Surface Technologies

Improvements in Water Heater Coatings
James Waters, A.O. Smith, Protective Coatings Division

Infrared Firing of Porcelain Enamel
Ralph Gwaltney, Maytag Cleveland Cooking Products

ISO 9001:2000 A Quality System for the New Millennium
Kara Joyce Kopplin, QTEC Consulting Corporation
Foreword

We are pleased to deliver to you this proceedings of the 65th Annual PEI Technical Forum. It represents the very successful completion of intensive planning and preparation, with three days of meetings, seminars, and plant tours at the Downtown Sheraton Hotel in Nashville, Tennessee, May 12-15, 2003. As you receive these proceedings, work has already begun on the 66th Technical Forum, to be held April 26-29, 2004, at the Downtown Sheraton Hotel in Nashville.

With the 2003 meeting, I completed my two-year term as chair of the PEI Technical Forum Committee, after two years of serving as vice-chairman. It has been a pleasure and a privilege to serve with the members of this dedicated and hard working committee, who put a lot of personal time and effort each year, into offering a first class program. I want to give special thanks to Steve Kilczewski (Pemco) our vice-chairman for the last two years, and to Jeff Wright (Ferro) chairman of PEI’s Technical Activities Committee for their continuous and creative support. The Technical Forum is in good hands as we look forward to next years program.

This proceedings continues the tradition of excellent papers given by experts in our industry, with high quality, informative presentations on many different areas of porcelain enameling. I believe we have continued the tradition of a program with something for everyone in our industry. In addition, Dr. Richard Lehman of Rutgers University returned to present a second A.I. Andrews Memorial Lecture on “The Structure of Glass - Part II”. Our thanks also go to the teams at Electrolux Home Products and Saturn Manufacturing, for their organization and coordination of excellent and informative plant tours on Thursday afternoon.

Once again, Holger Evele (Ferro) and Tony Mazzuca (Pemco) organized and coordinated a successful Back-to-Basics Workshop this year. This Workshop continues to be one of the best formats for introducing new industry members to porcelain enamel, and refreshing and updating more experienced members in the industry. We thank both Holger and Tony for their time and efforts in this ongoing endeavor.

This proceedings continues to be edited by William (Darry) Faust of Ferro, and we thank him again for his continued efforts.

Again, my sincere thanks to everyone involved in making the 65th Technical Forum a success. We urge all of you receiving this proceedings, to mark your calendars for next year’s event, April 26-29, 2004 in Nashville. I know that chairman Steve Kilczewski and the committee will produce another practical, and information-filled meeting.

Liam O’Byrne, AB&I Foundry
Chairman, 2003 PEI Technical Forum Committee
Lithium Minerals

Charles Merivale
Amalgamet Canada, Toronto, Ontario, Canada

This paper discusses the primary lithium resources in the world today, examines the special properties that make lithium valuable to porcelain and enamel and in ceramics in general, and concludes with a brief outline of other uses.

Introduction

Lithium is an interesting element that brings real value and benefits not only to traditional ceramic applications but also to porcelain and enamel. Helen MacInnes put it well when she said, “Nothing is interesting if you aren’t interested.” For those not familiar with lithium, my objective is to interest you in this element.

The words of General Douglas Macarthur — “There is no security on this earth; there is only opportunity” — suggest one reason to be interested in lithium: our world is changing so quickly today that old methods, used for generations in some cases, are under review, providing an opportunity to consider lithium in your formulas for the benefits it brings.

A final quote applicable to this paper references the reality that lithium is not an easy material to work with. Some less persistent ceramists have abandoned their efforts because lithium doesn’t follow straight-line performance but behaves differently in different applications under different environments, and generally require more than one test to reach the desired objectives. So Frank Clark’s warning that “a path with no obstacles probably doesn’t lead anywhere” is also quite appropriate.

Lithium fell just short of being a US$500 million business in 2001 and is expected to grow to over US$600 million by 2006 as new applications take hold. Lithium batteries — particularly the lithium ion battery — showed growth rates of 20–30% at the end of the 1990s as portable devices adopted lithium as a power source based on its ability to hold a charge for a long time. For our purposes, lithium is known as the most active flux for glass and ceramics, but the story starts with the sources for these very active ions and expands to many growing applications. One example we are all familiar with is thermal shock-resistant ceramics, such as Visions and Corningware cookware, which use lithium minerals’ beta phase conversion to
achieve the required thermal stability for open flame cooking pots as well as the oven-to-freezer ware made famous by Corning. One of the most exciting aspects to lithia is the eutectics formed with other fluxes, which create an even more favorable environment for lowering energy requirements as demonstrated by phase diagrams.

**Geology 101**

In assessing the sources of lithium, it makes sense to begin with nature and the processes that created not only lithium resources but all deposits mined around the world today. While we don’t have any eyewitness accounts to what transpired billions of years ago, scientists are quite confident in their theories of the origins of ore deposits and the processes of the evolution of rocks from magma to igneous to sedimentary to metamorphic. We now believe the earth is made up of tectonic plates floating on a magma sea surrounding a solid core. Movement of these plates causes earthquakes and periodically a volcanic event releases magma from depths of 200 km or more. This magma or molten rock contains primarily the elements necessary to form silicate minerals. Lava at the surface is an extrusive eruption, but not all eruptions reach the surface; some crystallize at depth, producing intrusive igneous rocks.

Igneous rocks are in turn classified into four main groupings, including basaltic and granitic, differentiated in part by the silica content. Different conditions surrounding the cooling or crystallization combined with the chemistry of the original magma determine the final chemical and physical characteristics of the resultant igneous rocks. Early in earth’s history, such volcanic eruptions were much more common than today, and their cooling rate seems to be the main determinant of the constituents found in any ore body. As heavier minerals cool in an intrusive magma body, they sink. Later in the cooling process, what has not crystallized can be enriched by rare elements and heavy metals. Pegmatites usually form at the edge of a larger granitic solidification and contain exotic minerals that did not go into the granite, forming numerous rare species. The complexity of the pegmatite increases as it moves away from the parent granite. Also, because water does not crystallize with the magma, conditions develop that favor large crystal growth, which also differentiates a pegmatite deposit. Pegmatites throughout the world are thought to range in age from 5 million to 2.8 billion years and are divided into two types: lithium cesium tantalum (LCT) type and niobium yttrium fluorine (NYF) type. The LCT type has
Table I. Comparative analysis of lithium minerals

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Theoretical Li,O%</th>
<th>Typical Li,O%</th>
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</thead>
<tbody>
<tr>
<td>Spodumene</td>
<td>LiAlSiO₆</td>
<td>8.0</td>
<td>4–7.5</td>
</tr>
<tr>
<td>Petalite</td>
<td>LiAlSi₃O₁₀</td>
<td>4.9</td>
<td>3.5–4.5</td>
</tr>
<tr>
<td>Lepidolite</td>
<td>K(LiAl)₃(SiAl)₂O₆(OHF)₂</td>
<td>4.1</td>
<td>3–4</td>
</tr>
<tr>
<td>Amblygonite</td>
<td>LiAlPO₄(FOH)</td>
<td>10</td>
<td>8–9</td>
</tr>
<tr>
<td>Montebrasite</td>
<td>LiAlPO₄(F₉)H</td>
<td>10</td>
<td>8–9</td>
</tr>
</tbody>
</table>

received more attention because of its economic value and consequent higher mining rate. While it goes without saying that each deposit is unique, hard rock pegmatite deposits can contain some of the least abundant elements and many different minerals, including spodumene, petalite, lepidolite, amblygonite/montebrasite, and eucryptite, in addition to tin, tantalum, beryl, cesium, quartz, rubidium, sodium, and potash — although not always in economically recoverable quantities or forms.

For example, while over 50 different minerals, including one new one, have been identified in the TANCO pegmatite in Canada, only three are being recovered today. Based on hundreds of drill holes, TANCO’s pegmatite deposit has been estimated at 2 km in length, having a maximum width of just over 1 km and a thickness up to 100 m, containing 25 million tonnes of ore. As a result of the conditions that created them, pegmatites are usually highly zoned; that is, individual elements are concentrated in specific areas enabling selective mining.

Sources of Lithium

Lithium makes up just 0.002% or 20 ppm of the earth’s crust, but many viable reserves have been identified by the U.S. Geological Survey, containing almost 13 million tonnes of contained lithium in the world. Roskill Information Services reports that world demand for lithium minerals and chemicals was 13 000–14 000 metric tonnes of contained lithium in 2001, and they project a growth rate of 2–4% through 2006. Lithium is currently extracted from both mineral and brine resources. Many minerals contain traces of lithium, but the primary ones mined for commercial use are amblygonite, spodumene, lepidolite, petalite, and montebrasite.

You can see in Table I that lepidolite, amblygonite, and montebrasite also contain fluorine, increasing their fluxing value. The lithia/alumina ratio...
in these minerals is consistent and lower lithia levels are compensated for by more silica. At present, spodumene is the dominant mineral supplied in North America, supplemented by some petalite. Lithium brines have become the major source for lithium carbonate production because of their lower conversion costs compared to hard rock lithium mineral resources. Lithium carbonate is the usual starting point for downstream lithium chemicals.

While production of lithium minerals occurs in several countries, international trade is limited to four significant lithium hard rock deposits as shown in Table II.

A large tailings pond at the TANCO mine in southeastern Manitoba serves the plant for cesium formate, the newest product for oil well drilling made from the largest known reserve of pollucite, the source of cesium. Underground work in the mine continues regardless of surface conditions. After a blast, the giraffe allows the miners to make sure no loose scale falls on those working below when they “muck out” the ore. The mining target in the TANCO pegmatite can be selectively chosen with a high degree of success and for our purposes today, spodumene blades are the subject of interest. No mine is complete without a laboratory facility, and TANCO’s has been supplemented to fulfill the requirements of cesium formate and every shipment leaving the site is assayed with the results supplied to our customers.

While there are many identified pegmatites in the world, economically viable pegmatites are rare because the ore quality, location, or size of the reserve may not allow for economic exploitation. Other pegmatites that have been developed and mined are in Brazil, Namibia, North Carolina, and China. Others that have been identified but not developed include many showings around the TANCO deposit, plus several in British Columbia, Quebec, and the Northwest Territories of Canada; South Dakota, California, and New Mexico in the United States; and in the Democratic Republic of Congo. For the most part these claims have lapsed, being too small to support long-term operations, or of poor quality, or because they are too far

<table>
<thead>
<tr>
<th>Company</th>
<th>Location</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bikita Minerals</td>
<td>Zimbabwe</td>
<td>Petalite/spodumene</td>
</tr>
<tr>
<td>Societe de Pegmatites</td>
<td>Portugal</td>
<td>Petalite</td>
</tr>
<tr>
<td>Sons of Gwalia</td>
<td>Western Australia</td>
<td>Spodumene</td>
</tr>
<tr>
<td>TANCO</td>
<td>Manitoba, Canada</td>
<td>Spodumene</td>
</tr>
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</table>
from the markets and low-cost transport options at a time when buyers are very concerned about delivered costs and have other options.

Today several companies are promoting their lithium supply potential, including one Quebec deposit being considered for lithium metal production. Another promising prospect is Avalon Ventures's Big Whopper deposit in northwestern Ontario. Avalon is developing a high-lithium feldspar pegmatite intended for glass, ceramic, and metallurgical applications. Some of you may remember the lithospar formerly offered from North Carolina; Avalon's product will be similar but with a higher lithium level. Piloting studies are now underway to establish the best processing methods to achieve the best product at the lowest possible cost. One slightly unusual feature of the Big Whopper pegmatite is that it appears very homogeneous across its length and depth. In a curious parallel program, this pegmatite contains such spectacular colors from the petalite and rubidium that it is also being considered for production of dimension stone, which may be the route to open the deposit by generating some cash, thus enabling construction of a mill and concentration plant.

Lithium is also found in salars, or dried lake beds, usually with other minerals that can be economically processed into lithium carbonate. Such salars concentrate lithium above 2000 ppm in some cases, which is the basis for production in Nevada and Chile by Chemetall, and SQM in Chile, using solar evaporation to progressively concentrate the lithium up to 6%. Chile's contribution to the lithium supply has grown from 6300 metric tonnes in 1994 to 11 900 metric tonnes contained lithium in 2001, which translates into an additional 25 000 metric tonnes of lithium carbonate. A comparable facility owned by FMC in Argentina is currently closed, keeping the market in balance. China is evaluating the development of several salars in Tibet and the western provinces, but these are some years away from startup although work has definitely started.

Historically, lithium minerals offered savings over chemical sources, but when SQM entered the market in 1996, prices fell significantly and the difference between chemical and mineral is no longer so great. SQM hopes to stabilize lithium carbonate around US$1/lb. When the Chinese projects come onstream, it is likely pricing will again come under pressure, although the timetable for these salar developments is unclear.

The largest identified lithium reserves today are in salars, but there is no shortage of mineral sources operating below their capacities worldwide. There is plenty of lithium available in various forms to suit all requirements and objectives.
Lithium appears near the top of the periodic table with an atomic weight of 6.9 (less than one-third that of sodium at 22.9) and an atomic number of 3. Lithium is the lightest of all solid elements with a specific gravity of only 0.5334; lithium metal floats on water or gasoline. Lithium has the smallest ionic radius and the highest ionic potential of any alkali (Table III). It is highly reactive and does not stay in its elemental form unless protected. Lithium is three times as powerful as sodium in fluxing potential. It also differs from sodium in that it creates favorable internal nucleation conditions, whereas sodium tends toward external nucleation. It raises the surface tension of glass and ceramics, whereas sodium and potassium reduce it. Lithium inclusions produce a microcrystalline structure.

The melting point of pure lithium is 180.5°C, but pure lithium is available only in metallic form, which is highly reactive and thus must be packed in oil. Lithium carbonate has a melting point of 720°C and spodumene’s melting point is 1420°C, which means it must be used in combination with other fluxes to activate the contained lithium and obtain a lower liquidus. The eutectics achieved with lithium and other fluxes are quite dramatic and worthy of experimentation in your formulas. The temperature composition projection of lithium and sodium oxides demonstrates how the eutectics of lithium and sodium work to lower melting temperatures. In some cases, only lithium carbonate might be suitable because of limits on alumina or iron, for example.

**Lithium’s Benefits to Glaze and Enamel**

Glaze and enamel are glassy materials, and so will be addressed under one heading. Specifics of the application may limit alumina or iron, in turn dictating use of lithium carbonate instead of spodumene, which may cause other issues. In both glass and ceramic applications, it has been said that lithium carbonate can cause outgassing problems as the CO₂ is released.

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**Table III. Relative ionic potential of lithium, sodium, and potassium**

<table>
<thead>
<tr>
<th>Element</th>
<th>Ionic radius (Å)</th>
<th>Ionic potential</th>
</tr>
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<tbody>
<tr>
<td>Lithium</td>
<td>0.60</td>
<td>1.67</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.95</td>
<td>1.05</td>
</tr>
<tr>
<td>Potassium</td>
<td>1.33</td>
<td>0.75</td>
</tr>
</tbody>
</table>
The relatively negligible increase in greenhouse gasses is less important than the potential effects on quality. In glass CO₂ can affect fining by causing more air bubbles; in ceramics it may show up as pinholes in the glaze or body. Mineral sources do not evolve CO₂.

Some of the following benefits overlap and may follow from body formula changes that include lithium to lower the firing times and temperatures, absorb free silica, or otherwise require a change in the glaze to match new body properties.

General ranges quoted for lithia additions to realize fluxing benefits would be as low as 2% spodumene or from 0.15% up to 2.5% Li₂O. As a flux lithia completely dissolves in the glass phase and reduces expansion as well as firing temperature and/or time. In glass formulas, we recommend only 0.22% Li₂O to achieve optimal benefits. More does not mean better in the case of lithium, but even though your glazes and enamels are glassy materials, your objectives could dictate other addition levels. Those of you who have worked with lithium in your glaze or enamel will recognize some of the following properties, but you may not have translated lithium into all its applications and benefits, which in some cases are consequences of other properties. In terms of the correct source to use, this is usually determined by a combination of chemistry and cost. In some cases the alumina that comes with the mineral is valued; in others it is a penalty and must be limited. And of course other mineral impurities sometimes cannot be tolerated. Generally, lithium for cover coat porcelain enamels tends to come from lithium carbonate because of limits on alumina and other impurities, but in ground coat applications, spodumene is preferred as a lower cost source.

Viscosity

Lithia lowers the viscosity of glass, giving better flow characteristics and permitting a thinner and more even glaze or enamel coating, which has benefits in controlling thermal expansion and crazing. A thinner coating will be less affected by changes in temperature and of course means that less is used, so more items can be handled in a comparable time period, resulting in cost savings from higher productivity. Lithia additions are also reported to improve opacity, assisting the thinner coating.

Luster/Brilliance

Lithia increases the luster and brilliance of glass and in glaze will enhance the color significantly. The brighter luster is the most commonly reported
effect from lithia additions after the viscosity change. In some cases, of course, this is not an advantage, for example, in the case of matching a historic color.

**Lower Maturation Times/Temperatures**
The high fluxing capability of lithium enables glazes or enamels to mature faster or at lower temperatures, or a combination of the two. This also translates into cost savings as more ware can be fired in less time or at lower temperatures to save on fuel costs.

**Low-Expansion Glazes**
Fast-fire low-expansion ceramics require low-expansion glazes, which can be produced with lithium additions. It is critical that the expansion of glaze and body are aligned to avoid crazing. Some glaze formulas show lithia contents from 0.5 to 25%.

**Lower Thermal Expansion**
Equal weights of lithium and other fluxes will provide many more molecules of lithium so less lithia can be used to reach the same effect. Combined with lithium’s inherently better thermal expansion characteristics, this means there is less potential for thermal expansion in a lithia-based glaze that contains a smaller total flux content.

**Improved Thermal Shock Resistance**
Similar to the comments on thermal expansion, contraction and expansion rates are based on the oxide weights in a glaze. Using lithium as the flux means the flux makes up a smaller proportion of the glaze compared to feldspar in this application, and therefore it allows a lower thermal expansion, improving the overall thermal shock resistance and reducing the potential for crazing.

**Lower Density**
Lithium silicate glasses have a lower density than other alkali surface glazes.

**Surface Tension**
In general terms, lithium has been shown to raise surface tensions of enamels. The mechanism just described, which permits a lower density, should also apply for glazes although there are contradictory accounts of this being