Chemical Composition of Scale in Maple Syrup Evaporators

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INTRODUCTION - As maple sap is concentrated into maple syrup, mineral deposits form within the evaporator. This naturally-occurring material can be broadly divided into two forms: sugar sand and scale. Sugar sand (also called niter or loose scale) is a precipitate that forms when the solubility of various elements in solution is exceeded. The resulting material is typically comprised mostly of calcium malate suspended in syrup (Heiligmann et al. 2006). The presence of sugar sand in unfiltered syrup results in a cloudy appearance, imparts an undesirable, gritty texture to syrup, and can result in an off-flavor if left in syrup over a period of time. Loose sugar sand is considered a nuisance by the syrup producer because it must be removed by some method of filtering before the syrup can be graded and sold. Past work has identified the variability in chemical composition of loose sugar sand (Snell 1914, Davis et al.1963, published in subsequent editions of the North American Maple Syrup Producers Manual). For example, previous investigations of loose sugar sand have observed the calcium malate content to range widely from less than 2% to as much as 85% (Snell et al. 1914, Willits et al. 1958). Chemical analysis of loose sugar sand shows the greatest single constituent of the material is generally calcium. One study observed calcium concentrations to range from as low as 0.61% to as much as 16.75% (Snell 1914). Warren (1911) determined calcium to be 17.14%. Earlier studies have identified a significant correlation between the calcium content in sap and the amount of sugar sand formed (Davis et al. 1963).

The second type of deposits, a persistent scale that is bonded to evaporator pans, presents additional challenges to the maple producer. This material is particularly problematic since it adheres tightly to the heated surface of evaporator pans, thus reducing heat transfer, resulting in a reduction of evaporator efficiency. Evaporators coated with scale are also at increased risk of overheating and damaging the pans (Heiligmann et al. 2006). Overheating presents the further danger of imparting a scorched sugar taste to syrup if scale is allowed to persist and the entrapped sugar burns. Removing scale from evaporator surfaces is difficult and time-consuming, therefore most sugarmakers resort to the periodic use of concentrated acid solutions (typically phosphoric acid) to dissolve the heaviest scale deposits.

A review of relevant literature revealed no published values on the mineral and metal composition of scale in maple syrup evaporators, or a comparison of the chemistry to that of sugar sand. Although it has yet to be documented specifically, loose sugar sand is probably derived, at least in part, from broken particles of scale. The goal of this work was to investigate the chemical composition of the scale that is deposited on maple evaporator surfaces during sap processing. Knowing the chemical composition of scale produced in modern equipment and how it compares to previously published values for loose sugar sand may aid in understanding how best to remove these unwanted deposits.

METHODS - Maple syrup producers were solicited to participate in this project via an email notice to North American Maple Syrup Council members. Producers who responded to the solicitation were provided with sample containers, datasheets, and were instructed to collect samples of scale from the front and back pans of their evaporator. Producers were not issued explicit instructions as to a method of sample collection. Producers recorded the date of collection, syrup production at the date of sample collection, evaporator fuel used, type of pan, and any other relevant information about their operation. Samples and completed datasheets were shipped to the University of Vermont Proctor Maple Research Center in prepaid mailers.

Samples were prepared for analysis by rinsing the scale with deionized water to remove loose and embedded sugar, followed by filtering (Millipore 0.45□m). The water and dissolved constituents were discarded while the solid fraction was retained for analysis. Rinsing and filtering the scale proved problematic for some samples. Samples that could not be filtered were discarded. The remaining samples were dried, then digested with standard laboratory protocols and analyzed at the University of Vermont, Agricultural & Environmental Testing Lab in Burlington, Vermont. The concentration of inorganic mineral and metallic elements in each scale sample [Calcium (Ca), Phosphorous (P), Potassium (K), Magnesium (Mg), Aluminum (Al), Iron (Fe), Manganese (Mn), Boron (B), Copper (Cu), Zinc (Zn) and Sulfur (S)] were determined by Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES).

RESULTS - The operations represented a diverse cross section relative to size of operation, sap collection methods and processing technology. The producers included operations ranging in size from 400 to nearly 60,000 taps. Samples were received from both bucket and tubing sap operations. Processing methods ranged from small, wood-fired evaporators boiling raw sap to large, oil-fired evaporators boiling highly-concentrated sap. Sugarmakers reported that samples provided generally represented a typical amount of buildup of scale, with a few reporting above (or below) average amounts. Some producers reported difficultly removing material from pans for samples.

Scale samples from the front and back pans of 17 maple syrup producers were analyzed for mineral and metal content. Six producers boiled concentrate and 11 boiled raw sap. Two producers reported collecting sap with buckets. The texture and consistency of samples varied from a nearly white sand to a dark, paste-like material (Figure 1). Scale samples similarly displayed a high degree of variability with respect to mineral and metal composition (Table 1).

By far the most abundant element was calcium (5.5-20.0%), followed by magnesium (0.61-2.73%) and phosphorus (0.74-2.13%). Manganese was the metal found in the highest concentration (0.90-2.80%). Aluminum, iron, and copper were present at roughly comparable levels. Zinc was intermediate. Potassium, sulfur, and boron were minor constituents.

In general, scale deposits from evaporators that processed sap concentrated with RO tended to have somewhat higher concentrations of minerals than the deposits from evaporators that processed raw sap. This is expected since these evaporators likely processed a greater volume of material overall than those processing raw sap. There were a few exceptions to this, however, and this may be related to the composition of collection and processing equipment used (as discussed below).

The concentration of some minerals and metals was higher than previously reported for loose sugar sand. Overall, the calcium concentration was higher in scale deposits than that which has been reported earlier for loose sugar sand (Davis et al. 1963). While Davis et al. (1963) reported similar levels of manganese and magnesium, the absolute concentration of manganese was higher in scale deposits than in loose sugar sand. Modern evaporators are constructed with stainless steel alloys that contain among other things, a sizeable amount of manganese. The higher concentrations of manganese in scale deposits may be caused by a combination of sap boiling in these evaporators and by sugarmakers scraping pans to collect samples. A similar situation may explain the higher than previously published values for boron. The evaporators used when previous studies of sugar sand composition were conducted (Davis et al. 1963) were likely made from galvanized steel and tin.

The methods of collecting sap and producing syrup have undergone sub-

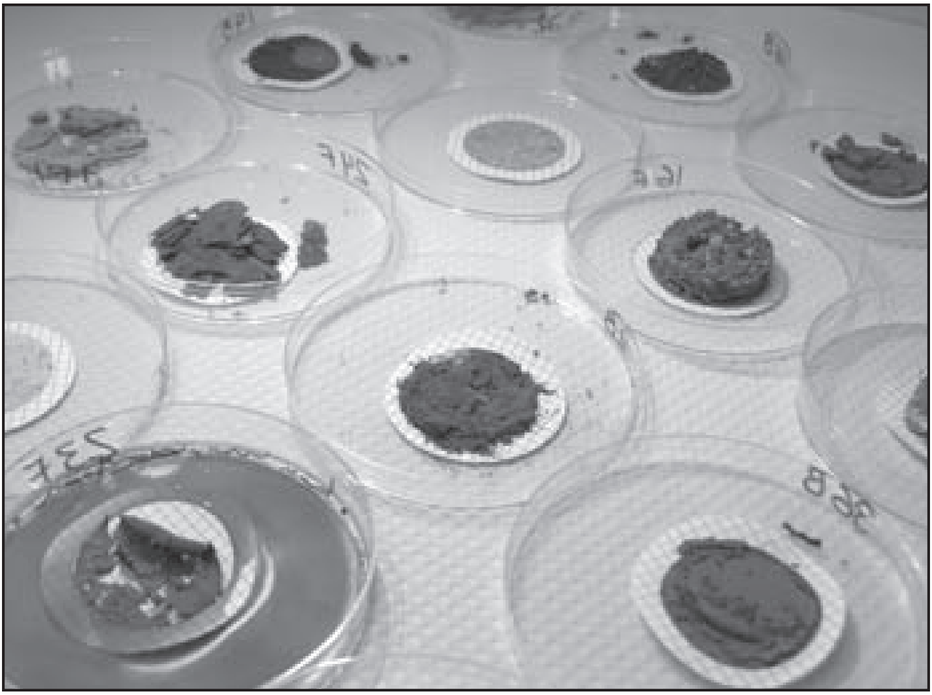

Figure 1: Examples of the texture and consistency of the solid fraction of maple syrup evaporator scale.

stantial changes in the last 50 years. The advent of vacuum extraction and membrane concentration of sap allow for greater yields and efficiency of maple operations. Although it appears high yield vacuum does not alter the mineral composition of maple sap (Wilmot et al. 2007), the composition of equipment (lead-containing buckets and evaporators for example) used to collect sap and produce maple syrup can have an impact on the finished product (Wilmot and Perkins 2000). It appears that operations that utilize bucket sap collection create scale deposits with higher zinc concentrations (Figure 2), probably derived from the zinc galvanizing in buckets. A similar result was observed for copper concentrations in scale samples collected from producers who used copper sap preheaters. Maple producers who reported using copper sap preheaters had higher copper concentrations in scale than those that did not employ this technology.

The results of this study suggest that the concentration of sap with RO technology may result in higher concentrations of select minerals in scale deposits. It is important to recognize however that the values reported here represent the concentration of various minerals remaining in the evaporator and do not necessarily reflect to the chemical composition of the finished syrup (Heiligmann et al. 2006). Considering that both loose sugar sand and scale are both formed during the boiling process, it is likely that they are made of the same constituents and therefore possess a similar chemistry.

Table 1. Concentrations of select elements in scale produced in the front and back pans of evaporators that boiled concentrated and raw sap. Values are means (+/- SE). N=6 for Concentrate, N=11 for Raw Sap.

		Back Pan		**Front Pan**		**Sugar sand**[1]
		Concentrate	Raw Sap	Concentrate	Raw Sap	Raw Sap
Ca	%	15.4 ± 4.4	5.5 ± 1.6	20.0 ± 2.4	11.3 ± 1.8	0.61 - 10.91
P	%	0.90 ± 0.34	2.13 ± 0.54	1.85 ± 1.70	0.74 ± 0.24	0.03 - 1.18
K	%	0.12 ± 0.07	0.05 ± 0.01	0.07 ± 0.03	0.09 ± 0.01	0.15 - 0.38
Mg	%	2.73 ± 1.22	1.92 ± 0.64	0.61 ± 0.34	0.83 ± 0.34	0.01 - 0.19
Al	%	0.06 ± 0.02	0.13 ± 0.03	0.04 ± 0.01	0.04 ± 0.01	na
Fe	%	0.10 ± 0.07	0.26 ± 0.11	0.04 ± 0.02	0.09 ± 0.02	0.004 - 0.1
Mn	%	2.01 ± 0.78	2.80 ± 1.24	1.87 ± 1.17	0.90 ± 0.40	0.06 - 0.3
B	%	0.009 ± 0.002	0.018 ± 0.002	0.007 ± 0.002	0.012 ± 0.002	0.0003 - 0.002
Cu	%	0.05 ± 0.02	0.19 ± 0.07	0.02 ± 0.01	0.16 ± 0.11	na
Zn	%	0.10 ± 0.06	1.82 ± 0.81	0.07 ± 0.02	0.56 ± 0.30	na
S	%	0.22 ± 0.04	0.23 ± 0.04	0.31 ± 0.05	0.21 ± 0.02	na

[1] Davis *et al.* 1963. Values are ranges, N=10

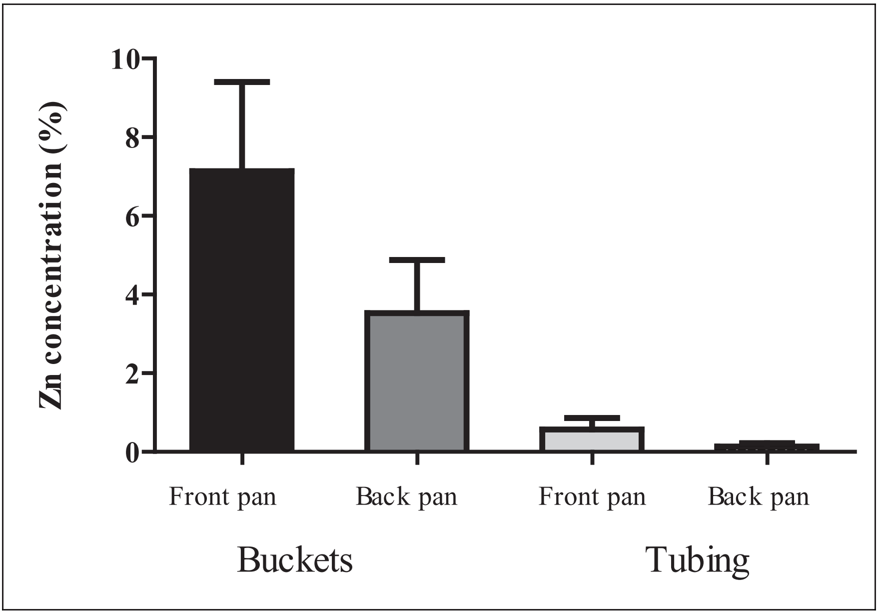

Figure 2: Zinc (Zn) concentration in mineral scale from evaporator pans (front and back) boiling sap collected with buckets and tubing. Values are means (+/-SE), N=2 for buckets, N=15 for tubing.

Effective syrup filtering and evaporator cleaning are key factors in producing a high quality product. Additional investigations that closely follow samples during processing as they transition from sap to syrup would be instructive in determining more precisely how collection and processing equipment influence the chemical composition of pure maple syrup.

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