A COMPARISON OF ANION CONCENTRATIONS ACROSS CARBONATION AT THE FIVE VALLEY FACTORIES OF AMERICAN CRYSTAL SUGAR COMPANY

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Introduction and Objectives:

A comparative study of the anion concentrations (malate, sulfate, citrate, phosphate and oxalate) across carbonation was undertaken at American Crystal Sugar Company (ACSC) in the fall of 2010. The objective of this study was to compare anion elimination between ACSC's five factories in response to the capture of oxalate scale in the standard liquor strainers at our Hillsboro (HLB), North Dakota, factory during the processing of MDS extract in August 2010. Poor elimination of oxalate in carbonation was initially suspected as the cause.

The results show that anion elimination at HLB met or exceeded the average elimination measured at the other four valley factories of ACSC. Current work has moved from assuming that poor oxalate elimination in carbonation is the cause to looking deeper into the chemistry occurring, including the possibilities of chemical precursors forming oxalate, a shift in the Na-K-Ca cation balance in the sugar end, and oxalate complexing with other chemical species.

Sampling and Analytical Method:

A total of 12 comparative surveys were undertaken – 2 each at Moorhead, Hillsboro and Crookston and 3 each at East Grand Forks and Drayton. Samples included: raw juice, cells at the beginning, middle and end of the prelimer, main limer, 1st carb juice, Dorr overflow (clear juice) and 2nd carb juice. Samples with suspended solids were filtered on-site and both the filtered and unfiltered portions were retained, being placed on ice for transport back to the ACSC Technical Services Center. The samples were then frozen if not analyzed the same day. The values reported in the Survey Results section and displayed in Figures 1 - 4 were obtained on the portions of each sample that were left unfiltered at the time of collection.

Analysis for malate, sulfate, phosphate, citrate and oxalate was performed using a Dionex DX-500 ion chromatograph with an AS11-HC column and guard, 30 mM NaOH eluent at a 1.5 mL/min flowrate in isocratic mode, and detection was done by conductivity with an ASRS300 suppressor installed. The samples were diluted, if necessary, and always filtered to 0.45 micron prior to injection.

Survey Results:

The comparative studies found that the carb elimination of the measured anions at HLB met or exceeded the average elimination of our other four Valley factories.
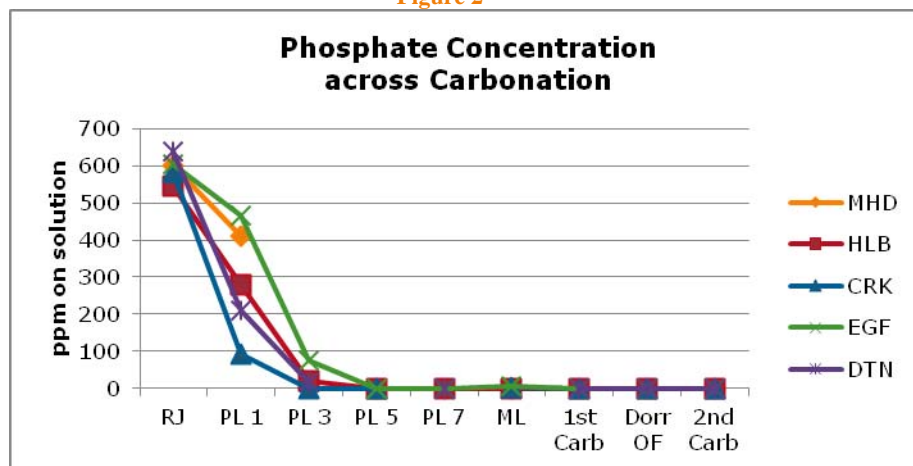
The average sulfate elimination at HLB was 61% versus an average of 52% at the other locations. Most of the reduction occurred in first carbonation (Figure 1).

Figure 1

Sulfate Concentration across Carbonation
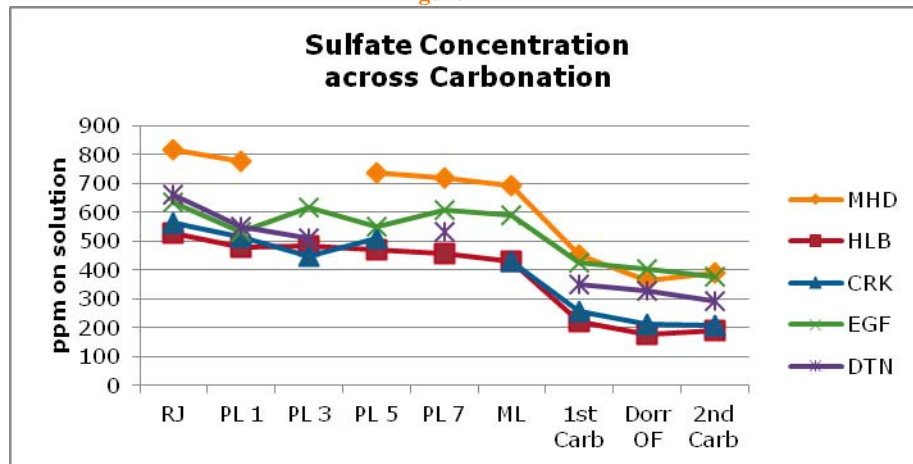
Complete elimination of phosphate was observed at all locations, with the bulk of the reduction occurring in Cell 1 of the prelimer with complete elimination by Cell 5 (Figure 2).

Figure 2

Phosphate Concentration across Carbonation

The average citrate elimination at HLB was 91% versus an average of 88% at the other locations. A slight decrease in citrate was observed across the prelimer and into main liming, but the bulk of the reduction occurred in first carbonation (Figure 3).

Figure 3

Citrate Concentration across Carbonation
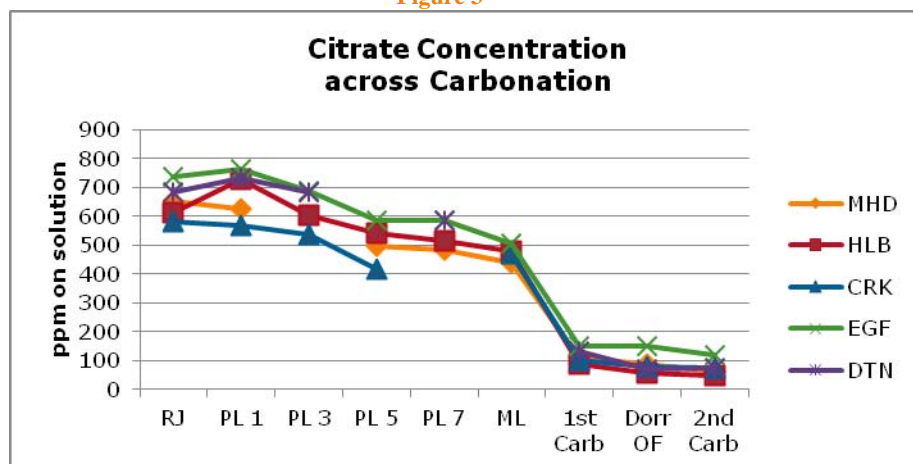
The malate results were invalid due to the co-elution of chloride with the malate anion in our analytical method. Since chloride is not eliminated in carbonation, it obscured the malate peak for all samples.

The average oxalate elimination at HLB was 99%, approximately equal to the other four factories' average of 98%. The bulk of oxalate precipitation occurs in the first cell of the prelimer with near-complete precipitation by Cell 7. However, we found that oxalate re-dissolved in the main limer and near-complete removal was achieved in carbonation (Figure 4).

Figure 4
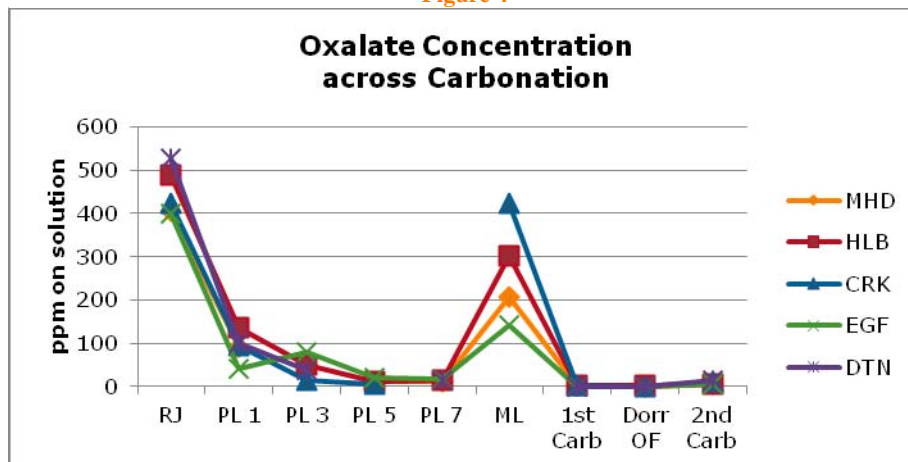
Oxalate dissolution in the main limer is mentioned in Beet-Sugar Technology[1], but we had prior data that both supported and refuted that. We found that the contradiction in our data may be due to filtration. Samples with suspended solids had been filtered through coarse paper during collection. Analysis of the filtered and unfiltered splits demonstrated that soluble oxalate decreased between 61% and 88% with filtration in the main limer sample (Table 1).

Table 1

Main Limer Sample Location – Date	Unfiltered Oxalate ppm	Filtered Oxalate ppm	Decrease
MHD – 11/11/10	194	36	81%
CRK – 11/11/10	496	60	88%
EGF – 11/16/10	148	57	61%
HLB – 11/18/10	359	46	87%
EGF – 12/3/10	88	17	81%

The other survey samples showed no appreciable difference in soluble oxalate concentration between filtration treatments (Figure 5, 11/11/10 CRK survey).

Figure 6
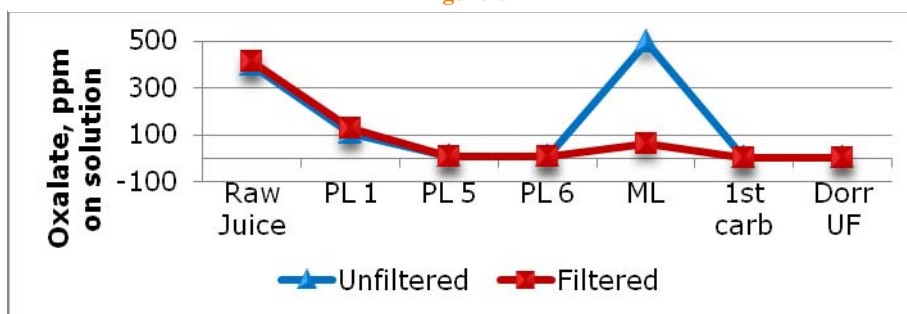
Comparison of the average ACSC anion elimination values obtained in this study show good agreement with values cited in the literature (Table 2).

Table 2

| Anion	ACSC Average Elimination	Sugar Technology, Table 2/34[2]		
		Carruthers	Reinefeld	Shiweck
Malate	--	48%	51%	65%
Sulfate	54%	63%		52%
Phosphate	100%	97%	99%	98%
Citrate	89%	92%	92%	97%
Oxalate	98%	ca. 100%	95%	98%

Oxalate Precipitation in the HLB Sugar End:

Precipitate formation reoccurred in the HLB sugar end during the processing of a blend of ~25% standard liquor and ~75% MDS extract in January 2011. The material was processed during a 12-hour scheduled shutdown and was brought into the beet end for color reduction through carbonation, which is standard practice at HLB. The precipitate was again captured in the standard liquor strainers and was identified as calcium oxalate by XRD analysis at North Dakota State University. The only successful fix during both the August 2010 and January 2011 events was physical removal of the material from the strainer during processing. The process flow surrounding the strainer is: standard liquor filters → concentrator supply tank → concentrator → flash cooler → **strainers** → white pan supply tank.

In searching for an oxalate source, we reviewed oxalate removal in carbonation, which was 99% at HLB in the fall surveys during beet processing and 99% during 30 gpm co-processing of the extract/standard liquor blend in February 2011. Additionally, there has been no reported scaling in the 3rd or 4th effects of the evaporator train.

The incoming oxalate values were also reviewed. The soluble oxalate levels in the extract produced at HLB are half that of thick juice; there is an average of 40 ppm oxalate on RDS in extract produced this campaign versus 80 ppm on RDS in thick juice. The low value in the extract is expected since 90% of the oxalate that enters the second loop of the HLB coupled-loop MDS system is rejected into the raffinate phase. In contrast, the extract produced from the non-coupled loop system at EGF has an average oxalate concentration of 230 ppm on RDS, and EGF does not process their extract with carbonation.

In the spring of 2010, the "secondary" molasses produced by the East Grand Forks factory during the processing of their extract into white sugar was processed at HLB MDS. East Grand Forks does not have a coupled-loop system and the resulting non-sugars distribution is different, which allows the secondary molasses to be processed through the HLB MDS plant. Concerned that oxalate may potentially be a problem, the levels were monitored in the feed molasses during this time. The soluble oxalate in the secondary molasses was in fact lower (average 190 ppm on RDS) than the typical virgin beet molasses fed to the plant at that time (average 310 ppm on RDS) (Figure 6).

Figure 8
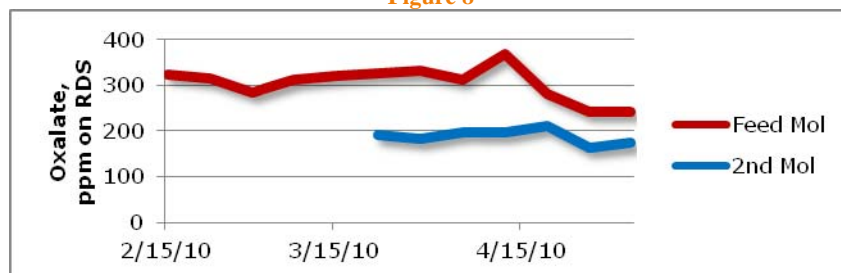
Possible Causes and Current Work

Since incoming oxalate levels don't appear to be the issue, other possibilities have been identified: chemical precursors, cation balance in the sugar end, and chemical interactions. Chemical precursors mentioned in the literature are glyoxylic acid, oxamic acid, oxamide, aconitic acid (not naturally occurring in beet but possible from the degradation of citrate) and allantoin[1,3].

Considering the cation balance, it may be possible that it shifts such that the calcium content is enough to precipitate the oxalate remaining after carbonation. As for chemical interactions, citrate is known to inhibit calcium oxalate formation in vivo[4] and other carboxylic acids are known to suppress the formation of calcium oxalate in the cane industry[5]. Perhaps there is applicability here.

Work to-date has involved trying to replicate precipitate formation in the laboratory. Bench-top carbonations of the extract were undertaken with no noticeable precipitate formation upon concentration. Calcium chloride addition did cause some turbidity and a slight reduction in soluble oxalate, but replication of those results is necessary. Adjusting the pH of the extract yielded no change in turbidity.

Our work moving forward involves identifying the mechanism of oxalate formation. We will measure samples across the sugar end for sodium, potassium, and calcium both with and without extract processing. Precursor analysis is an option through contract laboratories. Experiments will be designed with citric acid addition and with different cation concentrations. It has also been put forward that the oxalate scale may be pre-existing and not causing a problem until the low-oxalate extract is processed, knocking that existing scale loose. This may be determined by the use of metal 'coupons' placed in-line and measured periodically to quantify the deposition or removal of scale with time.

Conclusion:

We have moved from assuming that poor carbonation elimination is the culprit of oxalate scale formation during extract processing at our HLB factory to looking deeper into the chemistry occurring. Until the cause of this oxalate precipitation is found, we have recommended physical removal of the precipitate by increasing strainer capacity.

Acknowledgements:

Works Cited
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