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Helpful Information for You and Your Pool



Deep, Deep Dive into LSI and CSI

CSI and LSI - Further Reading

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CSI & LSI Development History

While this may be an oversimplification, LSI and CSI are practically the same thing.

LSI Development in the mid 1900's

LSI was developed in the mid 1900's by Robert Langlier. He was tasked by the water boiler industry to come up with a simple way to understand how water could become corrosive to metal pipes and how to predict if scale would occur. Using lots of empirical data and some science, he developed a scaling index (a mathematical formula that uses measurable parameters as inputs) to predict if water could become corrosive or scaling in terms of calcium carbonate. This was developed for closed-loop water boilers where you want water to be slightly positive in it's scaling index so a thin layer of calcium carbonate in your metal pipes would remain intact.^[1]

The problem was, a lot of the formula was developed based on empirical data and, since this was the 1940's, there wasn't a lot of accurate data for the fundamental chemical constants of various water constituents. As well, the LSI essentially used a "fudge factor" to account for the effects of high TDS and temperature. All of this was certainly fine to use at the time, but it was not based on fundamental derivations from chemical equations, what one would call "first principles".

LSI Adapted to be the CSI in the 1970's for the Pool Industry

Fast forward to the 1970's and a man by the name of John A. Wojtowicz comes onto the pool water scene and does a lot of fundamental scientific studies of various pool water chemistry issues. He also is responsible for much of the understanding of how cyanurates buffer chlorine which was originally developed in a scientific paper by O'Brien, et al..

Mr. Wojtowicz was dissatisfied with the LSI as a chemistry concept because there had been so many advances in the chemical knowledge since Robert Langlier's day and so he sought to develop, from first principles, the structure of a saturation index that would actually take into account all of the relevant chemistry with respect to the types of compounds one finds in pool water.

There are a series of papers at <u>*The Journal of the Swimming Pool and Spa Industry*</u>. In those papers, Wojtowicz outlines the derivation of the CSI and shows exactly how various factors like temperature and TDS come into play.

What Does the CSI or LSI Tell You?

The number one gets from a CSI calculation may be quantitatively different than an LSI number, but they essentially point to the same thing - water is either:

- balanced towards calcium carbonate- zero,
- scaling towards calcium carbonate positive
- corrosive towards calcium carbonate- negative

Calcium carbonate is one of the major materials in plaster surfaces.

LSI and CSI tell you nothing about the rates of scaling or corrosion, simply if it exists or not. It also has nothing to do with metal corrosion, ie rust, although people and the industry routinely cite LSI as a measure of metal corrosion (that is simply wrong).

Is CSI or LSI Better?

Do not get hung up on the "which is better" debate as that is a false-choice. The indices are simply measures of how stable calcium carbonate is in solution. You can use one or the other and both will give you the same general answer.

It's like saying my Snap-On wrench is better than your Craftsman wrench at tightening a nut & bolt...really, the wrench doesn't matter. Knowing how tight to make the nut is the more important bit of information.

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How is CSI or LSI Calculated?

CSI moves by the same amount that PH moves. So a 0.2 rise in PH results in a 0.2 rise in CSI assuming all else is constant.

PoolMath

TFP uses **PoolMath** to calculate CSI.

If you decide to post numbers and ask questions here, TFP would prefer you post a CSI value calculated using <u>PoolMath</u> to make it easier to help give advice.^[2]

Taylor Watergram wheel

This is another way to find the levels. It is included in most Taylor test kits.

What is the Science Behind the Langelier and Calcite Saturation Indices (LSI and CSI)? Much of the following is copied from the <u>JSPSI</u> addressing the issue of the applicability of the LSI or CSI.

Part of the problem is that the original LSI was modified (by someone unknown) for the pool industry. Whenever you see log terms for TDS and temperature dependence, these are approximations and not based the original thermodynamics (and yes, the Wojtowicz revision to the index has a log term for TDS).^[3]

These indices do nothing more than predict saturation of the water with calcium carbonate. If the water is over-saturated, then there is the possibility of scale, but the index does not determine its rate nor if there are seed crystals to get such precipitation or scaling started.

Likewise, if the water is under-saturated, then there is the possibility of dissolving of plaster, but again the rate is not determined and technically it is only the dissolving of calcium carbonate itself that would be possible.

These indices do not predict metal corrosion whatsoever. When one refers to water being "corrosive" in terms of these indices, it is only in reference to the dissolving of calcium carbonate as a component of plaster (plaster is mostly calcium oxide in a hydrated silicate). Technically, CSI is an indicator for scale and not etching although by extension there should

be a corollary to etching. Etching doesn't start at a particular CSI level but is related to the probability of occurrence. So a CSI of -0.6 would theoretically have twice the etching potential as a CSI of -0.3 (log scale) but both would still be extremely slow. Based upon some testing by on Balance, even a CSI below -0.6 showed very slow etching.^[4]

Articles Related to the Inapplicability of the LSI to Pools

Sources relating to the **inapplicability** of the LSI are here:

Cardall, John T. and Jonathan S. Powell Jr. "The Fallibility of the Langelier Index." Pool News (4 Aug. 1974): 40-43.

Cardall and Powell discuss the inappropriateness of applying the Langelier Index to swimming pools, and describe experiments which they conducted, refuting the validity of the index in the pool environment. They discuss some of the factors in the pool environment which interfere with the index.

Hamilton, Jock qtd. in Paul Konrad. "Whose Numbers Tell the Story?" Pool and Spa News (10 Apr. 1989): 22-26.

Hamilton is quoted in this story as refuting the Langelier Index's appropriateness in swimming pools, and offering an alternate index (the Hamilton Index) which he claims sufficiently addresses the pool environment.

Langelier, Wilfred F. "The Analytical Control of Anti-Corrosion Water Treatment." Journal of the American Water Works Association (AWWA) v28 #10 (1936):1500-1521.

This is the original paper published on the saturation concept, which has since become known as the Langelier Saturation Index. Langelier is cited as an associate professor of sanitary

engineering at UC Berkeley. The article contains formulas, tables, photographs, and references, as well as a history of study on saturation. The index is applied to municipal water piping systems. No mention is made to possible swimming pool applications of the concept.

Thomas, Jerome qtd. in Paul Konrad. "Whose Numbers Tell the Story?" Pool and Spa News (10 Apr. 1989): 22-26.

Dr. Thomas, successor to Dr. Langelier at UC Berkeley, is quoted in this article. He maintains that the Langelier Index "has no significance to open bodies of water" including swimming pools and spas.

Articles About the CSI for Pools

However, John A. Wojtowicz wrote several articles and did experiments showing that a true LSI (not the one the pool industry uses, but one similar to Langeleir's original and similar to my CSI) was **applicable**. Some of his articles are the following:

Swimming Pool Water Balance " Part 4: Calcium Carbonate Precipitation Potential"

Although the calcium carbonate saturation index is applicable to swimming pool water balance calculations, it is only a qualitative indicator of calcium carbonate precipitation since it does not indicate the extent of precipitation that can occur at positive values of SI.

Utilizing the mathematics of aqueous carbonate and cyanurate equilibria allows calculation of the quantitative calcium carbonate precipitation potential (CCPP), ie, the equivalent calcium carbonate supersaturation. Precipitation of calcium carbonate is accompanied by a drop in pH and a reduction in hardness of 1 mol and in total alkalinity of 2 equivalents for each mol of calcium carbonate precipitated. The calcium carbonate precipitation potential increases with saturation index and buffer intensity.

Buffer intensity in turn is a function of pH and total alkalinity. Because buffer intensity decreases with increasing pH, the CCPP also decreases as pH is increased.

Cyanurate contributes to total alkalinity, thus it inreases the CCPP for a given carbonate alkalinity.

At constant pH, carbonate alkalinity, and calcium hardness, the CCPP decreases with increasing TDS due to a decrease in SI.

In part 5 of this series, laboratory data on the precipitation of calcium carbonate under different conditions is presented and interpreted.

Swimming Pool Water Balance Part 5: Factors Affecting Precipitation of Calcium Carbonate

Laboratory tests with clear solutions showed that precipitation of calcium carbonate does not occur in the pH range 7.5 to 8.0 at alkalinities of 80 to 160 ppm and saturation indexes as high as 1.5. However, when the alkalinities are increased to very high levels, i.e., ~460 to ~325 ppm over the same pH range, evidence of precipitation was observed in the 0.5 to 1.1 saturation index (SI) range.

At typical swimming pool pH and alkalinity, seed crystals are necessary to initiate precipitation of calcium carbonate supersaturation. Suspended particulate matter can serve as seed crystals. Results of laboratory studies on precipitation of calcium carbonate in the presence of seed crystals are in general agreement with predictions based on the calcium carbonate precipitation potential (CCPP) model discussed in a previous article (Wojtowicz 1996). The results can be summarized as follows:

- at a given initial pH and alkalinity, the extent of precipitation increases with increasing SI,
- at a given initial pH and SI, the extent of precipitation increases with increasing alkalinity,
- at a given initial alkalinity and SI, the extent of precipitation decreases with increasing pH, and
- at a given initial pH, SI, and carbonate alkalinity, the extent of precipitation increases with increasing cyanuric acid concentration due to increased buffer intensity.

Swimming Pool Water Balance Part 6: Applicability of The Langelier Saturation Index to Swimming Pools

It is a common misconception that the Langelier Saturation Index applies only to closed systems because it was developed for water in distribution lines. Since it is based on calcium carbonate solubility equilibria, the Langelier Saturation Index is applicable to both open and closed systems containing dissolved calcium carbonate. The main difference is that in closed systems the alkalinity can vary at a given pH whereas in equilibrated open systems alkalinity is fixed at a given pH. In addition, since alkalinities are much lower in equilibrated open systems at comparable pH values, saturation hardness is much higher.

Another common misconception is that swimming pools are equilibrated open systems. Although swimming pools are open in a physical sense, they are not open in a thermodynamic (i.e., chemical equilibrium) sense. Swimming pools exhibit the characteristics of closed systems since they show the expected range and variability of alkalinity which is also typical of many public water supplies.

If swimming pools were equilibrated open systems (i.e., in equilibrium with atmospheric carbon dioxide), they would contain only 4 to 18 ppm alkalinity over the 7.2 to 7.8 pH range. At a given pH and alkalinity, swimming pools have the same concentration of dissolved CO2 as a closed system.

In order to attain equilibrium with the atmosphere, swimming pools would have to lose the excess carbon dioxide that they contain above the equilibrium value of 0.45 ppm. This will cause an increase in pH where higher alkalinities are allowed.

However, although swimming pools are open to the atmosphere, they never achieve equilibrium with the atmosphere because of acid addition, which in combination with continual carbon dioxide loss causes the pH to vary with time resembling a sawtoooth pattern.

Swimming Pool Water Balance Part 7: A Revised and Updated Saturation Index Equation

At a given temperature, swimming pool water chemistry must be balanced by adjusting pH, carbonate alkalinity, and calcium hardness in order to maintain the proper saturation with respect to calcium carbonate to avoid etching of concrete, plaster, and tile grout, scaling, and cloudy water.

Water balance is determined by means of the calcium carbonate saturation index (SI), which was originally proposed to provide corrosion control for iron pipes in public water distribution systems by means of deposition of thin films of CaCO3 (Langelier 1936). The current saturation index equation is based on calcium carbonate solubility data published in 1929.

This paper discusses revisions to the saturation index equation due to more accurate values for the calcium carbonate solubility product constant and its temperature dependence and more realistic ionic strength corrections. The revised equation is: SI = pH + Log[Hard] + Log[Alk] + TC + C where both hardness and alkalinity are expressed in ppm CaCO3, TC is the temperature correction, and C = -11.30 - 0.333LogTDS. The equation requires a reasonably accurate value of total dissolved solids (TDS). At 1000 ppm TDS, C is equal to 12.3. Above 1000 ppm TDS, this equation yields significantly lower values for SI than the current equation.

Swimming Pool Water Balance Part 8: The Thermodynamic Basis of the Saturation Index

Thermodynamics (i.e., the laws governing the conversion of heat to and from other forms of energy) is the logical discipline for the mathematical treatment of chemical reactions in homogeneous and heterogeneous systems. The sign of the free energy change as an indicator of the direction of a reaction was known in 1886 (Van't Hoff) under the name "œreaction isotherm". The free energy change is a measure of the useful energy available from a system.

When applied to solutions of calcium carbonate, the expression for the free energy change for a reaction readily and naturally leads to the calcium carbonate saturation index.

The equation that bears Langelier's name, derived from ionic equilibria, is not novel. Therefore, a more appropriate name would be calcium carbonate saturation index as Langelier originally named it (Langelier 1936).

Swimming Pool Water Balance Part 9: Corrections, Potential Errrors, and Significance of the Saturation Index

Calculation of the saturation index requires a knowledge of the water temperature and the concentrations of total alkalinity, calcium hardness, and cyanuric acid. Total alkalinity must be corrected for cyanuric acid present as cyanurate ion as well as the concentrations of other significant alkaline species.

In addition, the concentrations of complex forming ions other than bicarbonate such as sulfate and magnesium are required. Although these ions decrease the saturation index by reducing the concentrations of calcium hardness and carbonate alkalinity through ion pair formation, the effect is small except at very high levels of these ions.

Cumulative errors in typical swimming pool test kit analysis can result in a potential deviation in the calculated saturation index of ± 0.14 for water with 120 ppm total alkalinity, 300 ppm calcium hardness, and 100 ppm cyanuric acid.

The saturation index is not a corrosion index but rather a scaling index, ie, it is an indicator of the calcium carbonate scaling or scale dissolving tendency of water and not of corrosion.

- 1. <u>↑ https://www.troublefreepool.com/threads/langelier-and-calcite-saturation-indices-lsi-and-csi.4507/post-1413176</u>
- 2. <u>↑ https://www.troublefreepool.com/threads/langelier-and-calcite-saturation-indices-lsi-and-csi.4507/post-1445345</u>
- 3. ↑ <u>https://www.troublefreepool.com/threads/langelier-and-calcite-saturation-indices-lsi-and-csi.4507/</u>
- 4. <u>↑ https://www.troublefreepool.com/threads/thoughts-on-csi-and-fc.197158/#post-1738809</u>

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