Abstract—Evaluation and monitoring of physical and chemical water properties such as electrical conductivity (EC) and Langelier Saturation Index (LSI) are important in all industrial processes. Analytical representation of these water properties is useful since process modeling and simulation are exploited to investigate industrial system behavior under conditions that cannot be easily or safely tested. Common simulation softwares usually do not estimate the mentioned water properties but using literature information an estimation is possible through unconventional techniques. In particular Aspen Plus software has available calculator blocks to customize in order to represent specific features.

In the paper modelling of FORTRAN based calculator blocks are described, which have been developed using literature information to calculate electrical conductivity and Langelier Saturation Index in Aspen Plus software.

Keywords—Electrical conductivity; Langelier Saturation Index; Process Modelling; Process Simulation; Water Properties Evaluation and Monitoring

I. INTRODUCTION AND LITERATURE REVIEW

Water use is fundamental for many industrial processes; only suitable water quality allows the correct process operations and prevents undesirable phenomena like corrosion and fouling [1] [2].

Water properties evaluation and monitoring are fundamental in online measurement in order to avoid excessive water exploitation and frequent plant maintenance.

Nowadays exploration of industrial system behaviour under conditions that cannot be easily or safely tested requires ad-hoc developed studies, also supported by process modelling and simulation (PM&S) [3].

PM&S make possible in-depth investigation of future scenarios in order to evaluate the feasibility of process integration solutions [4] and multi-objective optimization to improve economic and environmental process sustainability according to [5] and [6]. Examples of PM&S applications can be the choice of the best industrial practice for a correct by-product and waste generation and management [7] or the minimization of freshwater consumption and wastewater generation [8] [9].

For this reason, in addition to online measurements, analytical representation of water properties obtains leading importance. However, many common simulation softwares do not estimate important physico-chemical properties such as electrical conductivity or Langelier Saturation Index (or require dedicated licences).

The present paper describes the development of FORTRAN based calculator blocks to evaluate above mentioned properties in Aspen Plus simulation software. After an introduction about electrical conductivity and Langelier saturation index, Section III gives information about the assumptions and the methods exploited in the modelling of EC and LSI calculators. Section IV concerns models validation and examples of applications. The last section is about the important and potential contribution that the developed models can have in process simulation.

II. FOCUS ON ISSUES

Electrical conductivity (EC) of water solution is a measure of its capacity to conduct electric current and it increases with temperature as the mobility of the ions increases [10]. Usually conductivity is linked with total dissolved solids (TDS) but it is important to consider that it does not take into account non conductive contaminants and therefore it is only a measure of electrolytes TDS.

Due to the EC dependence on concentration and nature of the ions, this variable is usually exploited in many industrial field (e.g. water treatment, desalination, leak detection, clean in place, interface detection) as a qualitative but not specific indicator of conductive ions content in a solution (Tab.I).

Langelier Saturation Index (LSI) is based on carbonate equilibrium in water and it is defined as [12]:

$$ LSI = pH - pH_s $$

where $pH$ is the actual pH of a water stream and $pH_s$ [13] the saturation pH of calcium carbonate based on the
TABLE II
WATER CHARACTERISTICS [14].

<table>
<thead>
<tr>
<th>Water Characteristics</th>
<th>LSI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly aggressive (corrosive)</td>
<td>$&lt;-2.0$ to $-0.5$</td>
</tr>
<tr>
<td>Slightly aggressive</td>
<td>$&lt;-0.5$ to $0.0$</td>
</tr>
<tr>
<td>Balanced</td>
<td>$0$</td>
</tr>
<tr>
<td>Nonaggressive (Protective film formation)</td>
<td>$0.0$ to $0.4$</td>
</tr>
<tr>
<td>Nonaggressive (Scale-Forming)</td>
<td>$&gt;0.4$</td>
</tr>
</tbody>
</table>

equilibrium expressions of calcium carbonate solubility and bicarbonate dissociation; the effects of temperature and ionic strength are considered.

Therefore, LSI represents the degree of saturation of calcium carbonate and its magnitude and sign are qualitative indicators of whether water will be corrosive or calcium carbonate will precipitate (Tab. II). If water pH is equal to \( pHS \) and \( LSI = 0 \), water is balanced. If LSI is positive, water is defined nonaggressive, it is oversaturated of \( CaCO_3 \) and scale-forming; LSI value in the range 0-0.4 shows a water tendency to inhibit corrosion with the formation of a protective film that insulates pipes and other plant components from direct contact with water. Finally, if LSI is negative water is corrosive (or aggressive) because it is unsaturated of \( CaCO_3 \), it will dissolve carbonates and prevents the formation of the protective carbonate coatings. In spite of its qualitative nature, LSI is a good medium in assessing water treatment requirements in industrial processes.

III. MODELS FOR EC AND LSI CALCULATION

Models have been developed using literature information about EC relationship with ion concentration and LSI relationship with alkalinity, calcium concentration, total dissolved solids and water temperature.

After the characterization of simulated water stream, import and export variables have been specified to allow the use of FORTRAN compiler. Modelling informations are now presented for each model developed: a calculator for electrical conductivity and two different calculators for Langelier saturation index (Fig. 1).

A. Modelling of Electrical Conductivity Calculator

Electric current is carried differently by cations and anions. Therefore in the modelling of EC calculator the conductivity factors for major ions have been considered (Tab. III).

The following approximate relationship is used in the FORTRAN compiler to obtain electrical conductivity in \( \mu S/cm \) [15]:

\[
EC = \sum C_i \cdot f_i
\]

where \( C_i \) is the concentration of ionic specie i in solution expressed in \( mg/L \) and \( f_i \) is the conductivity factor for ionic specie i.

Concentrations of ionic species are import variables for the model, while the conductivity factors have been inserted as constants in FORTRAN compiler. The export variable is the calculated value of electrical conductivity of water streams.

B. Modelling of Langelier Saturation Index Calculator

Langelier Saturation Index Calculator has been developed with two different approaches. In both cases the calculation of LSI from \( pH_s \) follows eq. (1) considering alkalinity, total dissolved solids, pH, temperature and calcium hardness. The first method (LSI-1 calculator) is based on a simplier relationship to calculate \( pH_s \) than the one used in LSI-2 calculator, where all the aspect that influences \( pH_s \) estimation are considered in detail.

Each model uses temperature, pH and ions concentration

<table>
<thead>
<tr>
<th>Ion species</th>
<th>Conductivity factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>2.6</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>3.82</td>
</tr>
<tr>
<td>K$^+$</td>
<td>1.84</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>2.13</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>0.715</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>2.14</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>1.54</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Figure 1. Electrical conductivity and Langelier Saturation Index Calculators in Aspen Plus.

TABLE III
CONDUCTIVITY FACTORS FOR COMMON IONS IN WATER [15].


where \( Z \) represents the oxidation number of the chemical species (\( Z = 1 \) for monovalent ions and \( Z = 2 \) for divalent ions) and \( I \) the Ionic Strenght of the water in \( \text{mol/L} \) (as in (13) with \( TDS \) in \( \text{mg/L} \)).

\[
I = 2.5 \cdot 10^{-5} \cdot (TDS) \\
\]

Some examples of applications of the developed water properties calculators are provided in the next section.

IV. Results

Validation of the calculator models has been carried out simulating different water streams and evaluating electrical conductivity and Langelier saturation index. The analyzed streams are listed below:

- fresh water A used in a steelmaking plant (FWA);
- fresh water B used in a steelmaking plant (FWB);
- process water of a steelmaking plant (PW);
- blowdown stream of a steelmaking plant (BW);
- sea water (SW) [14];
- tap water (TW) [14].

Water streams modelling has been carried out using laboratory or literature data about stream composition [14]. Results of EC and LSI calculators have been compared with laboratory data, literature informations or open source web calculator (OSC) results [14].

Table IV shows the following simulation data: absolute temperature \( T \) (K), water \( pH \), TDS (\( \text{mg/L} \)), alkalinity \( \text{Alk} \) (\( \text{mg/L} \) as \( \text{CaCO}_3 \)), calcium hardness (\( \text{mg/L} \) as \( \text{CaCO}_3 \)). EC (in \( \mu \text{s/cm} \)) data coming from laboratory tests (EC-Lab) and result values as output of developed calculator (EC-Calc) are compared in table V and in figure 2.

The EC calculator and laboratory values are similar; in the FWA case the error is higher than 5.5% but EC absolute value is comparable with laboratory data, which is related to water content of salts. The model reliability is proved.

<table>
<thead>
<tr>
<th>TABLE IV</th>
<th>SIMULATION DATA.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>300</td>
</tr>
<tr>
<td>pH</td>
<td>8.09</td>
</tr>
<tr>
<td>TDS</td>
<td>229</td>
</tr>
<tr>
<td>Alk</td>
<td>76</td>
</tr>
<tr>
<td>Ca hard</td>
<td>251</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TABLE V</th>
<th>ELECTRICAL conductivity results.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FWA</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>EC-Lab</td>
<td>330</td>
</tr>
<tr>
<td>EC-Calc</td>
<td>387</td>
</tr>
<tr>
<td>Error [%]</td>
<td>17.27</td>
</tr>
</tbody>
</table>

\[
\gamma_i = 10^{-1.82 \cdot 10^6 \cdot (78.3 \cdot T)^{-3/2} \cdot Z^2 \cdot \left( \frac{7}{7+i \pi} \right)^{-0.2 \cdot I}} \\
\]

\[
0.5M < I < 1M \Rightarrow \gamma_i = 10^{-1.82 \cdot 10^6 \cdot (78.3 \cdot T)^{-3/2} \cdot Z^2 \cdot \left( \frac{7}{7+i \pi} \right)} \\
\]

where \( i \) is an imaginary number.

\( I \) as input variables from water stream. Total dissolved solids are evaluated as the sum of all cations and anions referring to any minerals, salts, metals dissolved in water [16]. Alkalinity is expressed as the sum of bicarbonates and carbonates equivalents and it estimates the trend of water to neutralize acids as explained in [17].

1) LSI-1 Calculator: the method employed to develop LSI-1 calculator evaluates \( pH_s \) as (3) [18].

\[
pH_s = (9.3 + A + B) - (C + D) \\
\]

where \( A \) is the TDS (in \( \text{mg/L} \)) index, \( B \) is the absolute temperature \( T \) correction, \( C \) is linked to calcium hardness (\( \text{mg/L} \) \( \text{Ca}^{2+} \) as \( \text{CaCO}_3 \)) and \( D \) is the alkalinity (\( \text{Alk} \) as \( \text{mg/L} \) in \( \text{CaCO}_3 \)) index. The above listed quantities are evaluated as follows:

\[
A = (\log(TDS) - 1)/10 \\
\]

\[
B = -13.12 \cdot \log(T) + 34.55 \\
\]

\[
C = \log(\text{CalciumHardness}) - 0.4 \\
\]

\[
D = \log(\text{Alk}) \\
\]

2) LSI-2 Calculator: LSI-2 calculator exploits the following more complex equation to obtain \( pH_s \) according to [19]:

\[
pH_s = pK'_2 + pCa - pK'_s - \log(2 \cdot (\text{Alk})) - \log(\gamma_m) \\
\]

where \( pCa \) value is the negative common logarithm of the concentration of \( \text{Ca}^{2+} \) in \( \text{mol/L} \). Alkalinity (\( \text{Alk} \)) is reported as \( \text{mol/L} \) of \( \text{CaCO}_3 \). \( pK'_2 \) and \( pK'_s \) are the negative common logarithm of the activity constants \( K'_2 \) and \( K'_s \), which are expressed as:

\[
pK'_2 = -\log \frac{10^{-2902.39/T+0.02379T-6.498}}{\gamma_D} \\
\]

\[
pK'_s = -\log \frac{10^{-0.01183t+8.03}}{\gamma_D} \\
\]

respectively with temperature \( T \) in K and \( t \) in °C. Values of \( \gamma_m \) and \( \gamma_D \) are respectively the activity coefficient of monovalent and divalent ions, determined using the following Davies relationship:

\[
I < 0.5M \Rightarrow \gamma_i = 10^{-\left(1.82 \cdot 10^6 \cdot (78.3 \cdot T)^{-3/2} \cdot Z^2 \cdot \left( \frac{7}{7+i \pi} \right)^{-0.2 \cdot I}} \\
\]

\[
0.5M < I < 1M \Rightarrow \gamma_i = 10^{-\left(1.82 \cdot 10^6 \cdot (78.3 \cdot T)^{-3/2} \cdot Z^2 \cdot \left( \frac{7}{7+i \pi} \right)} \\
\]
On the other hand, table VI shows $pH_S$ and LSI results and figure 3 compares them: $pH_{-1}$ and LSI-1 and $pH_{-2}$ and LSI-2 are developed calculators results and $pH_{-OSC}$ and LSI-OSC derive from an open source web calculator [14]. Due to the qualitative nature of LSI, which gives an idea of water quality, it is possible to notice that model results are comparable. In most cases, each water sample falls within the same range of LSI (water quality) using the three different considered calculators. Gaps between absolute values can be justified by the lower accuracy of some used relationship or by lack of information about water modelled streams. In particular, as expected, method LSI-1 responds more rapidly due to reduced computational cost but with a higher error on the results.

V. CONCLUSION

In the current paper, the possibility of estimating and monitoring electrical conductivity and Langelier Saturation Index in Aspen Plus through FORTRAN based calculators has been presented.

Two LSI calculators based on different relationship in terms of accuracy have been described.

Both EC and LSI calculators have been validated.

Their implementation allows to control water contamination and its features in a complex process simulation, giving important informations that can support plant revamping or maintenance choice. For this reason, the realized water properties calculator models turn out to be important instruments in many process simulation studies.

### TABLE VI

$pH_S$ and LSI results.

<table>
<thead>
<tr>
<th></th>
<th>FWA</th>
<th>FWB</th>
<th>PW</th>
<th>BW</th>
<th>SW</th>
<th>TW</th>
</tr>
</thead>
<tbody>
<tr>
<td>$pH_{-1}$</td>
<td>7.60</td>
<td>7.43</td>
<td>8.81</td>
<td>8.89</td>
<td>7.96</td>
<td>8.21</td>
</tr>
<tr>
<td>$pH_{-2}$</td>
<td>7.56</td>
<td>7.53</td>
<td>8.94</td>
<td>9.00</td>
<td>7.89</td>
<td>8.17</td>
</tr>
<tr>
<td>$pH_{OSC}$ [14]</td>
<td>7.60</td>
<td>7.60</td>
<td>9.20</td>
<td>9.10</td>
<td>8.00</td>
<td>7.90</td>
</tr>
<tr>
<td>LSI-1</td>
<td>0.49</td>
<td>0.48</td>
<td>0.79</td>
<td>0.34</td>
<td>0.98</td>
<td>0.41</td>
</tr>
<tr>
<td>LSI-2</td>
<td>0.53</td>
<td>0.38</td>
<td>0.66</td>
<td>0.23</td>
<td>0.15</td>
<td>0.68</td>
</tr>
<tr>
<td>LSI-OSC [14]</td>
<td>0.53</td>
<td>0.36</td>
<td>0.41</td>
<td>0.10</td>
<td>0.05</td>
<td>0.68</td>
</tr>
</tbody>
</table>

### ACKNOWLEDGMENT

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### REFERENCES


