# Contamination of a Treating Solution with Caustic Soda
# Part 3: Charge Balances: Why and How to Do Them

In Parts 1 and 2 of this series, solution laboratory analysis interpreted using the results of an ion balance was used to show that the slowly deteriorating performance of a refinery, MDEA-based, tail gas treater was caused by leakage of caustic soda from another unit into the treating solution. In Part 2, simulation revealed the lab value of lean $H_2S$ loading should have resulted in better treating and, in fact, that a higher lean $H_2S$ loading was masquerading as thiosulfate. Using the corrected solution analysis, plant performance measurements were matched almost perfectly by ProTreat simulation. In this note, we focus on the ion balances themselves.

There is a multitude of heat stable salts (HSSs) present in many treating solutions, especially in refineries. Often these HSSs are neutralized with caustic soda or caustic potash, adding yet more ions to an already complex ionic soup. In addition, there is the potential for residual $H_2S$ loading to become oxidized to sulfate and thiosulfate by oxygen contamination of solution samples during handling and transportation. The net result is that unless samples are handled with great care to exclude oxygen at every step along the way, lean $H_2S$ loadings from direct laboratory analysis should probably be viewed with some suspicion. The problem manifests itself when process simulation is used to validate and analyze plant performance data because the lean solution loadings from lab analysis used in the simulation may be quite a bit lower than reality, leading to unrealistic performance expectations on the one hand, and poor agreement with test data on the other. The laboratory analyses themselves must be scrutinized carefully before simply entering them into a simulator. A useful way to do this is by checking each analysis against a charge balance.

The solution analyses presented previously are reproduced here in Table 1. Focus is on the January analysis as a specific example. Before getting started though, it's worth emphasizing that all ionic solutions must remain electrically neutral—the total concentration of positive and negative charges must be exactly equal. *Every solution analysis giving ionic concentration (usually via ion chromatography) absolutely must yield electro-neutrality; otherwise, it is in error*. So the first thing to do when you get a detailed solution analysis is to check that it obeys a charge balance.

**Table 1  Analyses and Absorber Performance**

| | Date of Sample | | |
|---|---|---|---|
| **Amine (wt%)** | **Jul** | **Dec** | **Jan** |
| Free | 37.6 | 42.6 | 47.4 |
| Bound | 2.5 | 2.1 | 0.5 |
| Total | 40.1 | 44.7 | 47.9 |
| **Ions (ppmw)** | | | |
| Sodium | **512** | **3831** | **7717** |
| Formate | 2,637 | 2,960 | 3,812 |
| Acetate | 2,270 | 2,542 | 3,322 |
| Chloride | 7 | 12 | 27 |
| Sulfate | 142 | 92 | 160 |
| Thiosulfate | 4,737 | 7,394 | 5,658 |
| Thiocyanate | 54 | 43 | 36 |
| **Total Anions** | 9,848 | 13,043 | 13,016 |
| DEA (wt%) | 2.6 | 2.0 | 1.6 |
| $H_2S$ load (m/m) | Trace | Trace | 0.0055 |
| **Meas. Absorber** | | | |
| $H_2S$ (ppmv) | **20–30** | **35–60** | **160–180** |
| $CO_2$ slip, % | NA | NA | 84–86 |

Step one is to convert all measured cations and anions into a consistent set of molar concentrations—mole fractions are used in this example. The conversion is done using an Excel®

spreadsheet[†] together with Excel's Solver function as follows. Referring to Table 2, the weight fraction of water (cell in blue) is made equal to one minus the mass fractions of all the other listed molecular and ionic components.

The mass fraction of acid gas species is not usually known from the solution analysis, at least not accurately. This is because the acid gases, which exist in solution as bisulfide and bicarbonate ions, result from weak acid ionization and do not show up with clarity in an ion chromatogram. In fact, an independent assessment of the total acid gas concentration is what the ion balance will provide. The $CO_2$ and $H_2S$ are present as single valence ions and we express the total mass fraction of acid gas in terms of $HS^-$ ion. Starting with an assumed value for weight fraction $HS^-$ (green cell in Table 2), the species molecular weights are used to convert mass to mole fractions (column 3), and then the valence of the ions is used to find the mole fraction charge contribution from each species (column 4). Mole fractions of all the charges must sum to zero; otherwise, the solution is not electrically neutral. Therefore, in the Excel sheet, Solver is used to force the value of the mole fraction total charge (red cell) to zero by adjusting the value of the mass fraction $HS^-$ ion (green).

**Table 2    Charge Balancing for January Analytical Data in Table 1**

| Amine | wt% | Weight Frac Species | Mole Frac Species | Mole Frac Charge |
|---|---|---|---|---|
| Free | 47.4 | 0.47400 | 0.12346 | |
| Bound (MDEAH$^+$) | 0.5 | 0.00500 | 0.00130 | 0.00130 |
| Total | 47.9 | 0.47900 | 0.12476 | |
| **Ions** | **ppm** | | | |
| Sodium (Na$^+$) | 7717 | 0.00772 | 0.01042 | 0.01042 |
| Formate (HCOO$^-$) | 3812 | 0.00381 | 0.00263 | –0.00263 |
| Acetate (CH$_3$COO$^-$) | 3322 | 0.00332 | 0.00175 | –0.00175 |
| Chloride (Cl$^-$) | 27 | 0.00003 | 0.00002 | –0.00002 |
| Sulfate (SO$_4^=$) | 160 | 0.00016 | 0.00005 | –0.00010 |
| Thiosulfate (S$_2$O$_3^=$) | 5658 | 0.00566 | 0.00157 | –0.00313 |
| Thiocyanate (SCN$^-$) | 36 | 0.00004 | 0.00002 | –0.00002 |
| **Other Components** | | | | |
| Acid gas as HS$^-$ | | **0.00433** | 0.00407 | –0.00407 |
| Water | | **0.49593** | 0.85471 | |
| **Total** | | | 1.00000 | **0.00000** |

The result is that the mole fraction total acid gas required to satisfy electroneutrality is 0.00407 and with a known total amine mole fraction of 0.12476, the total loading is 0.00407 / 0.12476 = 0.0326 mol/mol. This is *six times* higher than the lean $H_2S$ loading reported by the laboratory for the January sample. However, this example calculation is just a little more complicated than this because there is actually more sodium in the January sample than is required to neutralize the HSSs, i.e., there is more than enough to return all the amine to its unprotonated, or free, state. The last column of Table 2 shows that the mole fraction charge on sodium (0.01045) is greater than the sum of the charge mole fractions on the HSSs (0.00765). This means the HSSs are completely neutralized so, no matter what the lab analysis says, the bound amine concentration is in fact zero. The charge balance will have to be rerun. But first, consider the sulfate and thiosulfate ions.

As discussed in Part 2, these species are probably the result of oxidation of residual $H_2S$ in the lean amine samples. *Precautions are rarely, if ever, taken to exclude air from sample bottles when the sample is taken, transported (usually with great agitation), and analyzed—**but they should be**.* Thus, the real amine sample probably contains little or no sulfate and thiosulfate so their values in Table 2 should also be zero. Now when the spreadsheet is rerun the mole fraction acid gases necessary for electroneutrality is 0.00592 and the loading is 0.0474 mol/mol—an $H_2S$ loading more than 8 times the lab value! As shown in Part 2, this thinking was completely validated by ProTreat simulation where simulated performance was an $H_2S$ leak of 162 ppmv and 86.9% $CO_2$ slip versus measured values of 160–180 ppmv and 84–86%.

During troubleshooting, a complete solvent analysis is a much more valuable asset that might meet the eye. But the solvent analysis can and should be checked for consistency. The Excel spreadsheet described here is very easy to set up and, once created with all possible HSSs included in the template, it can be used as a standard tool for validation. Until such validation is done, any laboratory analysis of lean solution $H_2S$ loading should be viewed with considerable skepticism.

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