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Chemical analysis of process water for bitumen extraction from oil sands

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Process Diagnostics

26 April 2012

Canada

Abstract

Canadian Natural Resources Limited (CNRL) has determined that the extraction rate of bitumen from oil sands could be improved if the chemical composition of the water used in the froth floatation process could be monitored online. In addition, the measurements would help increase the recycled fraction of process water and reduce fresh water consumption. Therefore, the goal of this project is to measure the Na, Ca, Mg, and K concentration in process water. The measurement technology that was selected is laser-induced breakdown spectroscopy (LIBS).

Currently, CNRL plans to install a filtering system that will extract water from the line and remove all traces of bitumen and solid particles. Consequently, a first goal of this project is to measure the concentration of the four elements in clear filtered water. However, the filter may not work adequately and there could be other locations where it would be desirable to measure the concentration of these elements in water. So this project addresses also the objective of measuring poorly filtered or unfiltered process water. The effects of different types of particles are considered.

The concentration of the four elements of interest was measured in various systems: simulated process water, real process water, de-ionized water with controlled additions, and a model system of de-ionized water containing NaCl in solution and spinel particles in suspension. These experiments, the LIBS technology, the results obtained, and the conclusions that were drawn are detailed in this report.

1. Introduction

The Canadian oil sand industry is under economic and environmental pressures to improve the efficiency of bitumen extraction from oil sands. Canadian Natural Resources Limited (CNRL) has determined that process efficiency could be improved if the chemical composition of the water used in the froth floatation process could be monitored. Optimal concentrations of several soluble elements can increase bitumen recovery efficiency. In addition, the online measurements of these elements would help increase the recycled fraction of process water and reduce fresh water consumption.

In response to this need, this project's objective is to develop an online sensor that can measure in real time the concentration of four elements, Na, Mg, Ca, and K, in solution in the process water. To do so, Laser-Induced Breakdown Spectroscopy (LIBS) sensing technology will be used.

LIBS consists in producing plasma with an intense laser pulse and analysing the light emitted by the plasma with a spectrometer to obtain atomic composition. The advantages of LIBS are that it does not require sample preparation, it can be automated easily, and it is equally applicable to solids, liquids and gases. These qualities are making it a technology of choice for real-time monitoring of chemical composition during materials processing. Other analytical approaches for the determination of the concentration of these elements in water, such as atomic absorption spectroscopy (AAS), inductively-coupled plasma (ICP) spectroscopy, optical emission spectroscopy (OES), and ICP mass spectrometry (MS) are not useable online. X-ray fluorescence analysis (XRF) can be used for online monitoring. However, the technique is not sensitive to low Z elements such as Na and Mg.

Objectives

The objective of this project is to measure the concentration of four elements, Na, Mg, Ca, and K, in solution in process water before bitumen is extracted by froth floatation at CNRL. The expected concentration range and the required measurement accuracy are listed in Table 1. Of these four elements, it is far more important to obtain the concentration of sodium. Potassium is the least important of the four measurements.

Table 1. Soluble elements, their concentration range, and the required measurement accuracy for the LIBS sensor.

Element	Range (wt ppm)	Relative target accuracy
Na	750-2000	5%
Mg	0-20 (200 max)	10-20%
Ca	0-20 (100 max)	10-20%
K	10-200	10%

At the measurement location, the process water is a mixture of water, bitumen, air, and solid particles. CNRL plans to extract some water from the pipe and filter it. The filtered water should be clear of bitumen and solids. The filtered water will be analyzed for its pH

using a commercial meter, and for soluble elements concentrations using our LIBS sensor. The filter was designed to provide very clear water, free of particles. Therefore, it is required that the LIBS measurements work on well-filtered water. However, it is very difficult to build such a filter. Bitumen is known to cause problems when flowing in pipes. Moreover, the filter lifetime is unknown. Therefore, another goal of this project is to measure the solute element concentration in poorly filtered or, ideally, unfiltered water.

LIBS technology

Briefly, Laser-Induced Breakdown Spectroscopy uses a pulsed laser to ablate samples and a spectrometer to analyze the resulting light. The laser light pulse typically lasts 10 ns and contains 200 mJ of energy. When focused onto a surface, the laser beam vaporizes a small amount of material and turns it into ionized gas, called plasma. The light emitted by the plasma is analyzed with an optical spectrometer and provides information on the atomic composition, as well as molecular fragments of the vaporized material or surrounding atmosphere. The LIBS technique has well-known advantages compared to other analytical methods. The most relevant are that sample preparation is not necessary, and only tiny amounts of sample (typically a fraction of ng or less) are used. The method can be applied to liquids, gases, and solids. Finally, contact with the sample is not necessary, sample preparation is usually not necessary, and analysis can be made at a distance in hostile or sterile environments with the use of optical fibers or optical systems such as telescopes. This technique is simple, produces results within a minute, can be automated, can be portable, provides multi-element detection in a single shot, and does not require extensive operator training. It is sensitive to practically any element in the periodic table.
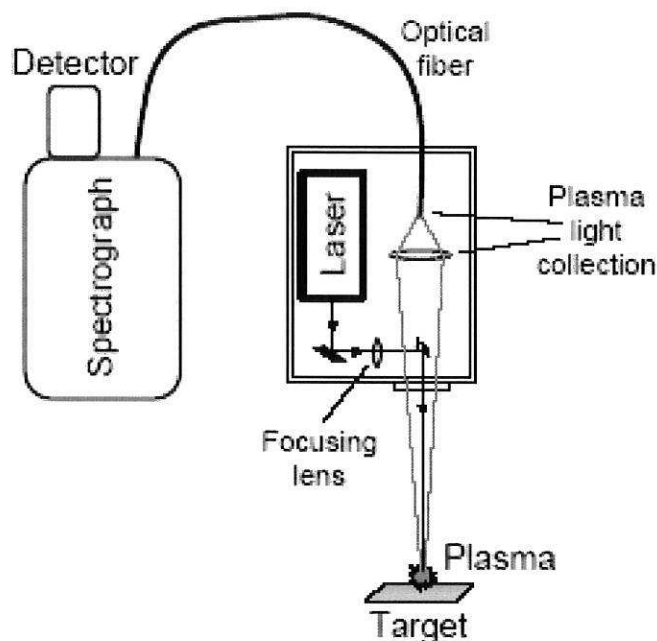

Figure 1. Schematic representation of a typical LIBS experimental set-up

2. Experimental setup

LIBS measurements of aqueous solutions differ a little from measurements on solids. Water-based plasmas have shorter duration and are not as hot, thus providing less light. The ablation process can cause suspensions of water droplets in air, or of air bubbles in the water, both of which can interfere with laser-matter interaction and with the measurement and its stability. Experience in our group, as well as in another research group, indicates that LIBS measurements on water samples are best done on a free-flowing, vertical water column. This is illustrated in Figure 2. Water is pumped into a funnel. The funnel acts as a reservoir that dampens pumping oscillations. The LIBS measurement is made a short distance from the bottom of the funnel. There, the water is free flowing, has not gained much vertical velocity, and has a stable free flow. The free-falling water "jet" is then collected in a small basin or a second funnel and returned to the top funnel in a closed loop. One advantage of this setup is that, if there are particles in suspension, the mixture will be constantly re-homogenized, thus preventing possible segregation and time-varying results.

The pulsed laser optics and the plasma light collection optics can be either co-linear, or not. The optics may be centered or not with respect to the jet axis. We use a small offset so that the ejected plume of plasma and water droplets does not go back onto the optical components.

The LIBS hardware employed a Q-switched Nd:YAG laser providing 1064 nm infrared pulses of 200 mJ of energy, and 8 ns duration. The beam was focused using a lens of 25 cm focal length. In general, it was found that it was best to focus the beam several mm behind the surface. This increased the area of the beam at the surface, making the plasma plume larger, and increasing the amount of water vaporized before the beam becomes completely blocked by the plasma (plasmas are good conductors and therefore good reflectors).
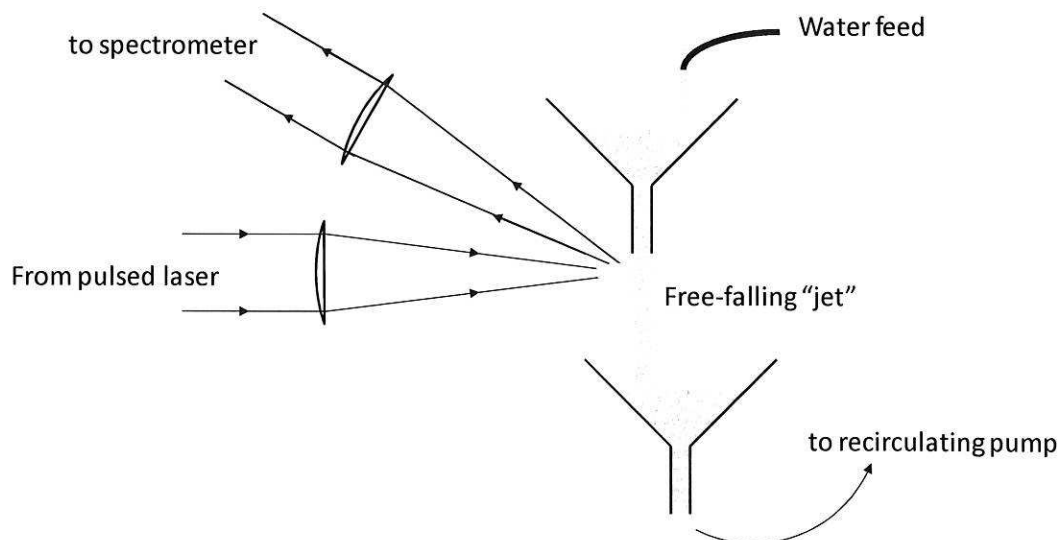

Figure 2. Schematic representation of the circulation system for LIBS measurement of process water.

The plasma light was collected using a corrected triplet lens of 2.5 cm diameter, 4.5 cm focal length and refocused onto a fiber of 600 μm diameter. This fiber was then butt-coupled to a fiber bundle containing 14 fibers of 100 μm diameter. The bundle was split into two bundles of 7 fibers that went to two different spectrometers. The 7 fibers of each bundle were aligned and behaved as the entrance slit of their respective spectrometers. One spectrometer was a Czerny-Turner type spectrometer (SPEX model 340, with a grating of 600 grooves/mm) equipped with an iCCD camera (Andor model iStar 720DH with 256 x 1024 pixels). The camera allows for precise time-resolved measurements where the opening and closing time of the intensifier can be set with a precision of approximately 1 ns. This spectrometer offers a higher resolution window covering the 475 to 595 nm portion of the spectrum where the Na line and the H_β line of hydrogen can be found. The other 7-fiber bundle was sent to a compact Czerny-Turner spectrometer (Avantes model Avaspec-2048). This spectrometer is equipped with a linear CCD array of 2048 elements. It provides a low-resolution, wideband spectrum from 225 to 775 nm. This compact spectrometer allowed the simultaneous measurements of all elements of interest, but without the time-resolving capability of the other spectrometer.
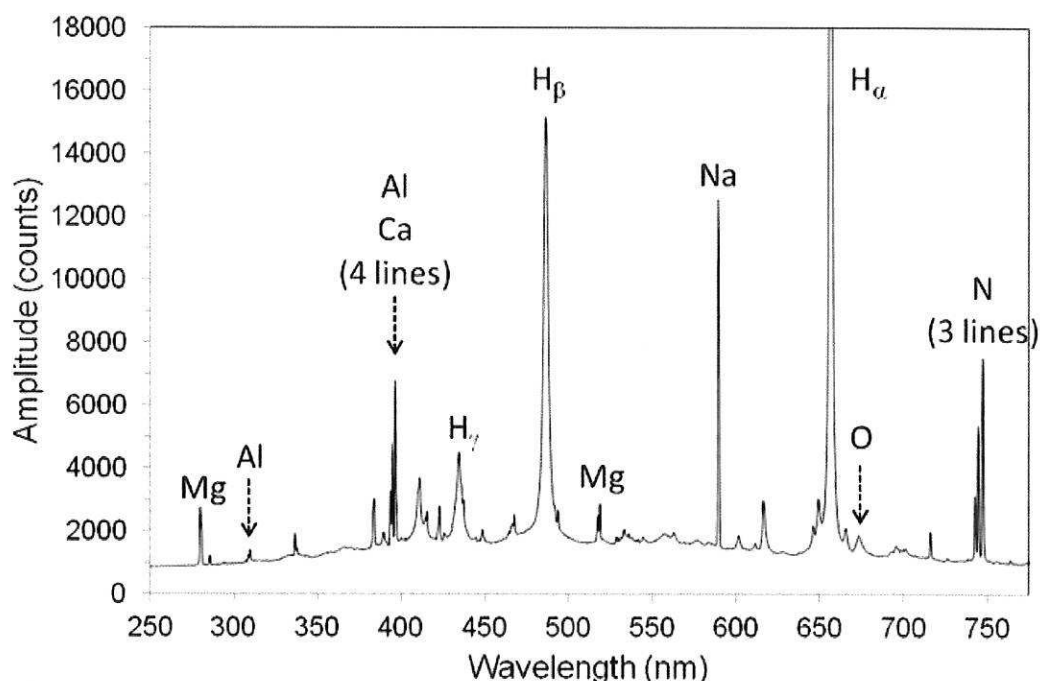

Figure 3. Wideband spectrum of water containing a solution of NaCl and a suspension of $AlMg_2O_4$ particles.

An example of the wideband spectrum is shown in Figure 3. This spectrum was acquired on a model system sample consisting of water containing a solution of NaCl and a suspension of $MgAl_2O_4$ particles. This model system will be discussed in details later in this report. For the purpose of this illustration, we note that all of the elements present in water (H, O), air (O, N), in solution (Na), and in the particles (Al, Mg, O) can be detected. The spectrum also shows a group of 4 lines (that can be separated if the spectrum is enlarged around 390 nm) that are cause by Al and Ca (2 lines for each element). Ca is a very common impurity and contaminant and was likely added together with the solid particles. Also, the spectrum displays only a weak oxygen line at 672 nm. It is possible to

adjust the spectrometer to capture the strong oxygen triplet a 777 nm, but because oxygen is present everywhere (air, water, solid oxides), the oxygen lines are not very useful. The sodium line is a doublet that cannot be resolved with the spectrometer. The H_α line is very large and saturates the detector. Therefore, hydrogen is measured using either the less intense H_β or the H_γ line. Finally, the potassium lines cannot be observed in this spectrum since no potassium was added. The spectrum shows that all characteristic lines (except for potassium) have large enough amplitudes to be easily measurable. Table 2 details the characteristic wavelengths and energy levels of all emission lines used in this report.

Table 2. Emission lines used in this report, and their basic characteristics. Ionic lines are indicated with a "+".

Element	Lambda (nm)	Low E (cm^{-1})	High E (cm^{-1})
H_α	656.280	82259	97492
H_β	486.134	82259	102823
H_γ	434.049	82259	105291
H_δ	410.176	82259	106632
H_ε	397.010	82259	107440
Na	588.995	0	16973
Na	589.592	0	16956
Al	396.152	112	25347
Al	394.400	0	25347
Al	308.215	0	32435
Al	309.284	112	32435
Al	309.271	112	32436
Ca+	393.370	0	25414
Ca+	396.850	0	25192
Mg	285.210	0	35051
Mg+	279.550	0	35760
Mg+	280.270	0	35669
N	742.396	83285	96751
N	744.264	83319	96751
N	746.860	83366	96751
K	766.491	0	13042
K	769.897	0	12985
O	394.728/394.747	73768	99095/99093
O	672.649	73768	88630
O	777.196	73768	86631
O	777.418	73768	86627
O	777.540	73768	86625

3. Measurements on water without solids

Limits of detection

Measurements on water containing only soluble elements were made by several authors. IN this project such measurements were made to estimate the limit of detection, i.e. the smallest detectable amount, of our experimental setup with respect to the four elements of interest.

To do this, the line amplitude of the corresponding element was measured as a function of concentration in standard solutions based on de-ionized water. For each sample, an average of 50 spectra is made to improve signal-to-noise ratio. The limit of detection is defined as the concentration corresponding to a line amplitude of three standard deviations above the background.

The results are shown in Table 3. Clearly, the system can detect Na, Mg, and Ca easily in their respective ranges of concentrations. For K, the limit of detection is the same as the lower limit of the concentration range. Therefore, K is much more difficult to measure precisely.

Table 3. Limit of detection of the soluble elements. The expected concentration range is given for comparison.

Element	Range (wt ppm)	Limit of detection (wt ppm)
Na	750-2000	10
Mg	0-20 (200 max)	0.6
Ca	0-20 (100 max)	0.5
K	10-200	10

4. Measurements on water containing a suspension of solids

Simulated process water sample set

The process water to be characterized is an aerated slurry of water, bitumen, sands and clays at 60 °C. Bitumen is highly viscous. In the process, it can flow because of the elevated temperature and its mixture with air and water. At room temperature, it clogs pipes and it is very difficult to handle. So to facilitate our work, and because CNRL plans to use and online filter to produce clear water, we experimented on filtered simulated process water, free of air and bitumen.

The simulated process water samples were made by CNRL by mixing together water, bitumen-free oil sand, and Na-rich "drop" water. The water was then filtered using three different filter sizes. Table 4 shows the parameters used. A complete matrix of 45 samples was made (5 levels of oil sands, 3 levels of drop water, 3 levels of filtering, for a total of 5 x 3 x 3 = 45 samples).

Table 4. Parameters used in fabricating the 45 samples of simulated process water.

Parameters	Levels
Oil sand	8, 9,10,13,14 %
Drop water	0, 5, 10 %
Filter size	0.1, 0.45, 20 μm

Two thirds of these samples were then analyzed by CNRL to obtain the concentration of the four elements in solution. All but three of the 45 samples were also sent to Agro-Enviro-Lab (AEL) for the same analysis. Both measurements were made by inductively-couple plasma spectroscopy (ICP-OES). The measurements from both companies correlated very well but showed systematic differences. An example is shown in Figure 4 for the measurement of Na where it is seen that the CNRL measurement is systematically higher than the AEL measurement. As a result, any LIBS correlation obtained by comparing the LIBS line amplitude to either of these laboratories may be off by some systematic amount. Such correlation would show that LIBS measurements do work; on the other hand, they might be improperly calibrated. Therefore, another means of calibration is required. We will see in the next section that this was provided by another series of 6 samples consisting of de-ionized water into which was dissolved precisely weighted amounts of NaCl.
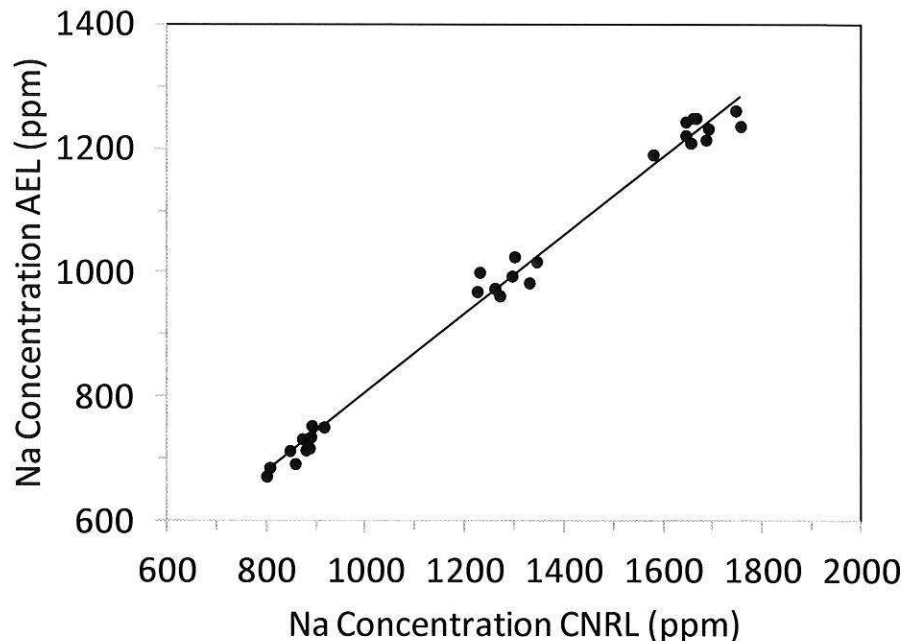

Figure 4. Sodium concentration in simulated process water samples measured by two different laboratories.

The rms residual of the correlation shown in Figure 4 is 21 ppm on an average (AEL) concentration of 1000 ppm. This represents a measurement precision of 2.1%. Because we do not know which of the two is better, if a correlation is obtained between a LIBS

measurement and one of these two ICP measurements to a level approaching 2% relative, or 21 ppm absolute with the AEL measurements, then we will have achieved the best possible correlation.

Because nearly all samples were measured by AEL and only two thirds by CNRL, AEL measurements are used in this report.

LIBS measurements on simulated process water

The amplitude of the sodium line was measured for all simulated process water samples. More often than not, in LIBS, it is preferable not to measure the absolute value of an emission line, but to measure its ratio with a line from the matrix. This helps eliminate some experimental errors such as the shot-to-shot variability in the plasma light intensity. In this report, the only element that can serve this purpose is hydrogen because it is the only element present in water (the matrix) that is not present in air. However, hydrogen is not a good choice because the energy levels of the transitions are far from the energy levels of the other elements of interest. To this day, it is still not clear whether it is better to normalize by a hydrogen line or to not normalize at all. In order to not duplicate every figure, unless otherwise noted, we have decided to present only line amplitudes that have been normalized by the H_β line.

The normalized Na line amplitude (i.e. the Na to H amplitude ratio) of 42 simulated process water samples is plotted against the Na concentration as measured by AEL in Figure 5. Although there is some overall correlation between the two axes, the amplitude ratio does not permit to measure Na concentration to within the objective of 10% relative accuracy. On the other hand, Figure 5 also includes 5 samples of de-ionized water in which precisely weighted amounts of NaCl were added, and one sample of pure de-ionized water. A linear least squares fit through those 6 points shows that the line amplitude ratio provides an excellent estimate of the Na concentration for these samples. In addition, the fit seems to match some of the data points from the process water.

Several factors were studied trying to figure out why some process water samples matched the aqueous solution samples, and other samples did not. Some of the results pointed towards the filter size used (0.1, 0.45, or 20 μm), but in the end, none of the parameters used in building the sample set (oil sand, drop water, filter size) allowed to select those points that did or did not agree with the aqueous solutions.
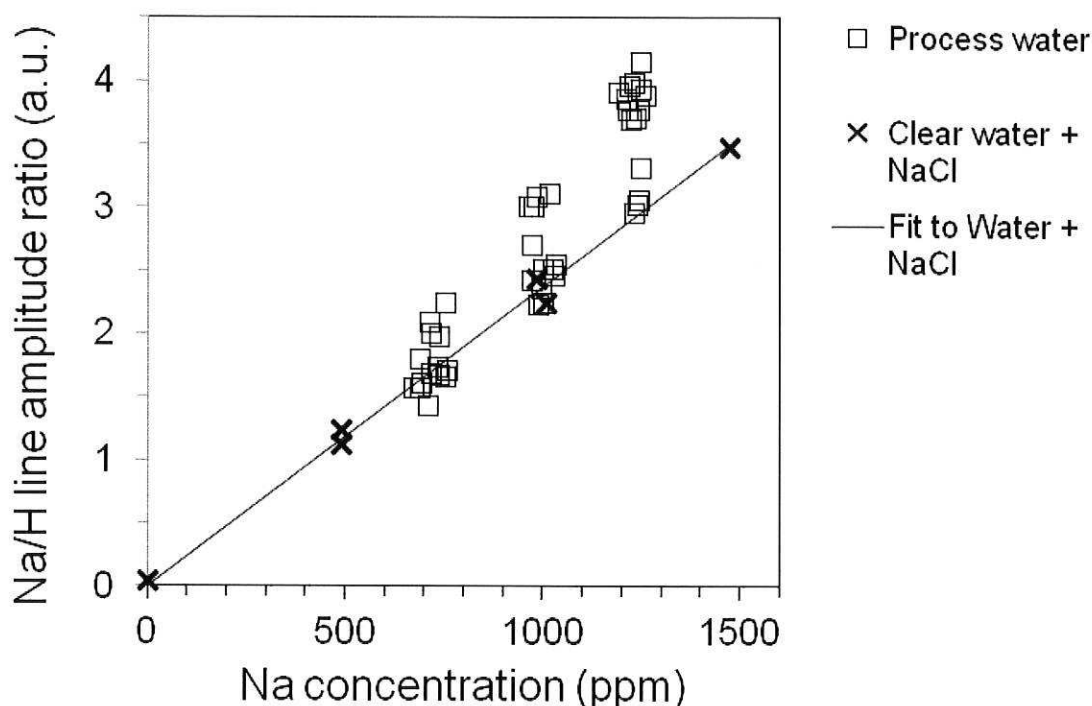
Figure 5. Normalized Na line amplitude ratio for 42 simulated process water samples (solid dots) and 6 samples of NaCl aqueous solutions (X symbols) as a function of Na concentration. The solid line is a linear least squares fit to the water + NaCl samples.

Measurements on model system

We needed to understand why the simulated process water samples behaved differently from the clear aqueous solution. We reasoned that the most likely factor that could affect plasma generation would be the solid particle content. Solid particles could change the penetration depth of the laser radiation either by increasing absorption or by trapping the radiation near the surface by way of multiple scattering. In addition, it would be important to know if the solids turn into plasma in measurable quantities, which could affect the species and the concentrations observed in the plasma and cause a matrix effect. Perhaps, the solid particles contributed more to the plasma than the water itself.

We immediately realized that to model the complexity of the simulated process water would be intractable and so we settled on a simple model that might capture the essential physics. We decided to incorporate insoluble spinel particles and completely soluble NaCl salt to de-ionized water. The NaCl would provide the Na ion that we are trying to measure, while the spinels would not provide any Na and would model the effect of solid particles on plasma generation. Among the various insoluble particles that could have been chosen, we selected spinels. Spinels have the chemical composition $MgAl_2O_4$. If they are transformed into plasma, they will be easily detected from the Mg and Al emission lines, with the additional advantages that Mg is one of the elements that we are trying to measure, and Al is a common element in clays. The particles that were introduced had a diameter less than or equal to 44 μm.

Table 5. Parameters used in fabricating the model system consisting of a solution of NaCl and a suspension of $MgAl_2O_4$ particles in de-ionized water.

Parameters	Levels
Na	0, 500, 1000, 1500 ppm
$MgAl_2O_4$	0 - 4%

This model system was used to optimize various experimental factors (focal length and position of lenses, position of plasma with respect to the water jet, camera delay and integration time, the effect of gas flow, laser power). Our goal was, in addition to better understand the effect of particles on plasma generation, to find a configuration that would provide a Na emission line that would be stable and as sensitive as possible to Na concentration while being as insensitive as possible to spinel particle concentration.

The final configuration employed a laser focusing lens perpendicular to the water jet and a plasma light collecting lens about 30° above the plasma generation lens. The laser beam was focused only a few mm below the funnel and slightly off center so that splashing droplets would not come back onto the laser lens. Gas flow had no effect on the measurement. Measurements near the edge of the jet (as opposed to slightly off center) seemed to produce equally good results, but were discarded because near center measurements are more robust against small optical misalignments. This final configuration is also that which was employed in producing Figure 5.

While measuring the sensitivity of the setup to spinel concentration, an important result was reached. Figure 6 shows the (absolute) emission line amplitude for Na and H as a function of spinel concentration. Figure 7 shows the ratio of those two lines, again as a function of spinel concentration. The two figures show that the Na and H line amplitudes as well as their ratio are very sensitive to a small addition (0.05%) of spinel to the spinel-free water. After an initial sharp drop, the line amplitudes increase back to a higher value just as rapidly. Beginning at around 0.5% spinel concentration, the amplitude becomes nearly constant. The amplitude ratio rises sharply initially and returns to the spinel-free value at spinel concentrations of 0.5% and above.

Another important result obtained with this model system is that Mg and Al lines were always present, independently of spinel concentration (except zero, Figure 8) and experimental configuration. We could not, for example, focus the laser beam to a tight spot to probe a small volume and so observe Al and Mg lines on some spectra and not on others, depending on whether or not a small particle was present in the small volume that was probed. Instead, the spinels always contributed to the plasma. The size distribution of the particles was not measured and so we do not know the number density of the particles. From these observations, we can conclude qualitatively that it is likely that clay particles in suspension in process water will contribute to the plasma, just as the spinels did.
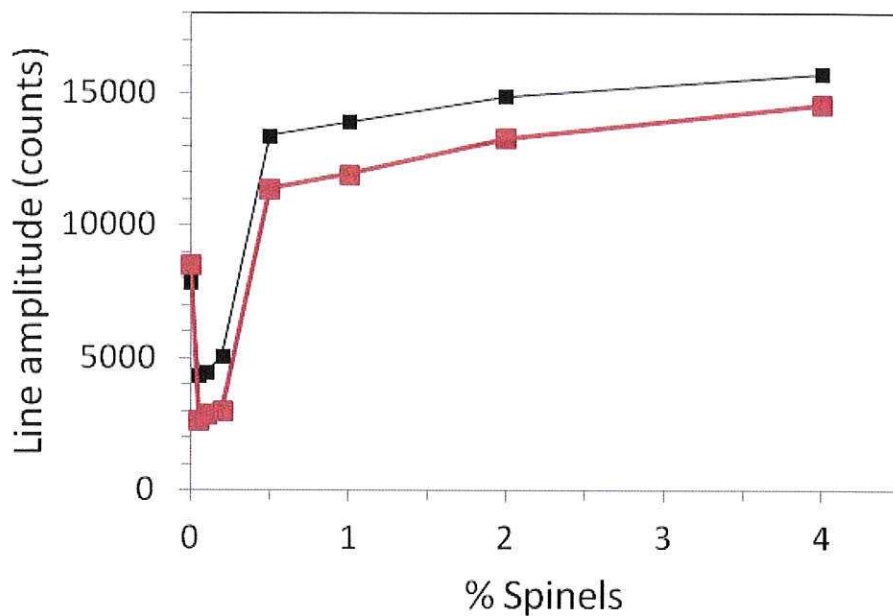
Figure 6. Na (black squares and line) and H_β (red squares and line) emission line amplitude as a function of spinel concentration.
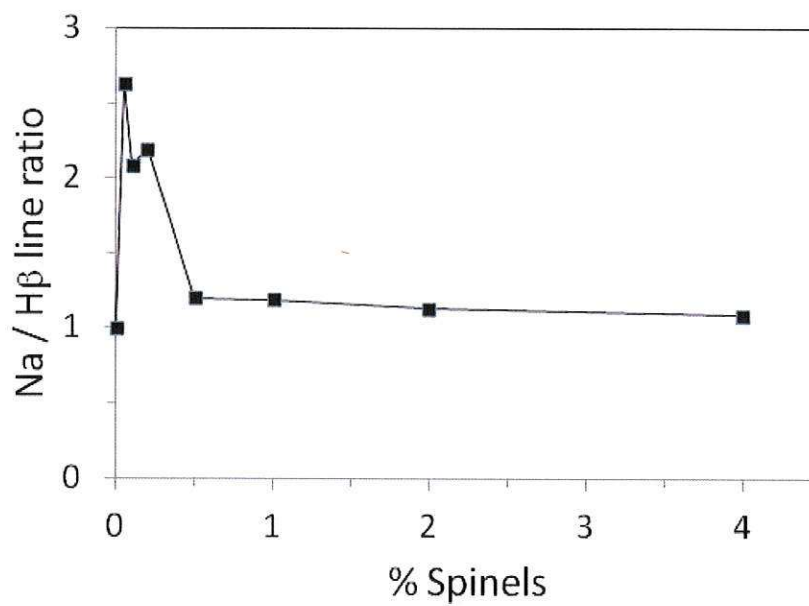

Figure 7. Ratio of the Na to H_β line amplitudes as a function of spinel concentration.
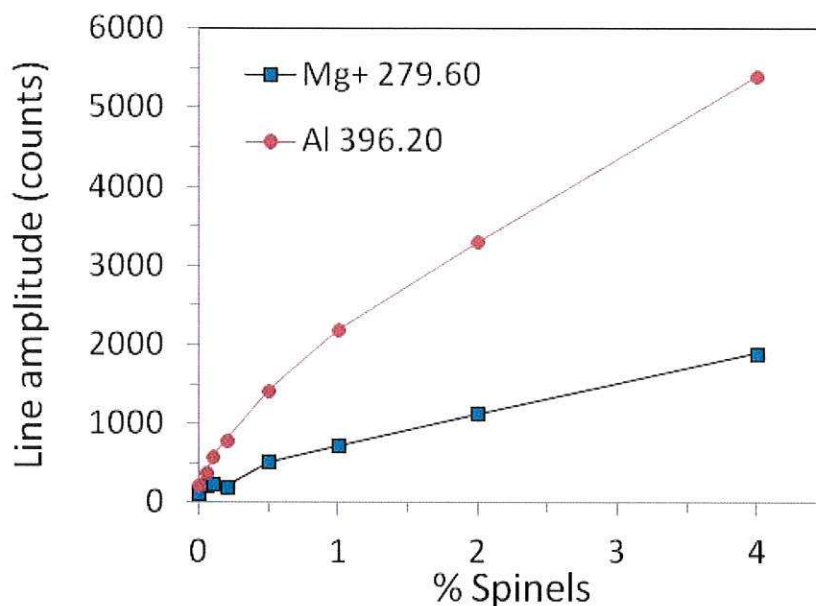
Figure 8. Aluminium and Magnesium emission line amplitude as a function of spinel concentration.

The colour effect in simulated process water

Figures 6 showed that, when water contained 0.5% or more spinels, line amplitude was nearly independent of spinel concentration. One possible explanation is that, as particles are added to clear water, laser penetration depth decreases, initially very rapidly, and later much more slowly, possibly as the inverse number density of particles. When the penetration depth is shallow enough, the laser energy is deposited closer to the surface, resulting in plasma that would be somewhat different, at least at the location probed by the lens that collects the plasma radiation. We estimated plasma temperature by comparing the H_β and H_γ line amplitudes. The results suggest that plasma temperature is higher when spinel concentration is 0.5% or more.

Figure 9 shows four plastic containers containing the model system sample with 4% spinels (left), and three samples of simulated process water of light, medium and dark colours. Spinels are transparent. In the form of a suspension of particles, they diffuse light. Thus the suspension looks white. The simulated process samples contained oil sand particles that were dark, so they diffuse and absorb light, giving some colour to the samples. If we assume that the spinel effect is caused by a reduction of laser penetration depth as the concentration of spinels increases, then perhaps sufficiently dark simulated process water behaves in a manner similar to the model system, that is perhaps the Na line amplitude depends on colour for light coloured samples and does not depend on colour for sufficiently dark samples.

The simulated process water samples were ranked from lightest to darkest colour. Many times, the colour difference was difficult to evaluate and ranking errors are possible. We then ranked the amplitude of various emission lines and compared the amplitude ranks to the colour ranks. Good correlations were obtained with the oxygen line at 394.3 nm and with the nitrogen line at 746.9 nm (Figure 10). Oxygen and nitrogen are constituents of water and air and are not expected to vary with the concentration of soluble elements

or elements contained in the solids. So we concluded that colour did indeed affect the plasma. In fact, darker samples correlated with more intense lines, which may indicate that plasma temperatures of darker samples were higher at the detection location.
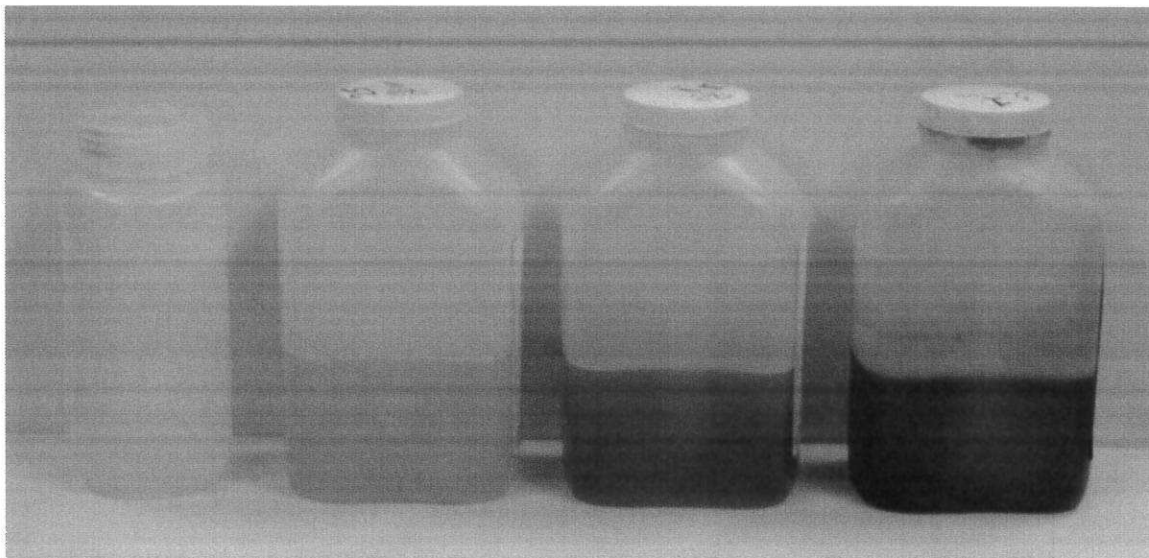

Figure 9. From left to right, model system containing 4% spinels and simulated process water of light, medium and dark colour.
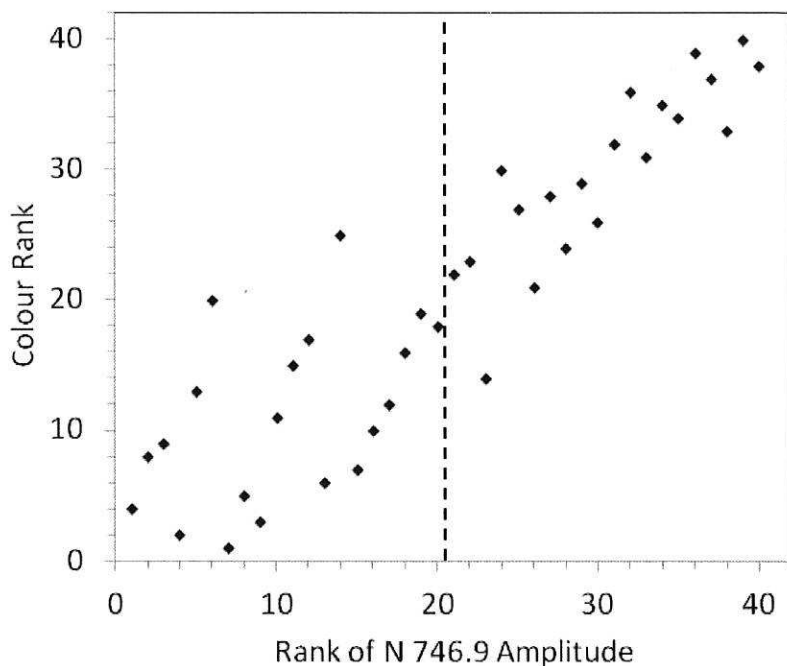

Figure 10. Correlation between the colour rank (1 is lightest colour, 40 is darkest) and the rank of the 746.9 nm nitrogen line amplitude. The dashed line separates the data in the two groups that are used to construct Figure 11.

Because the colour ranking was somewhat subjective, the amplitude rank of the N 746.9 nm line was then used as a more objective proxy for colour rank. Then Figure 5 was re-plotted but, this time, the simulated process water samples were grouped into those with lighter and darker colours (Figure 11). The threshold was selected by trial and error. The correlation between the line amplitude ratio and the Na concentration is much better if only the darker samples are retained. Moreover, the clear samples made from a solution of NaCl into deionised water and the darker samples have the same amplitude ratio as the darker samples at constant Na concentration. This is analogous to the model system with spinels where the sample without spinels had the same amplitude ratio as the samples with 0.5% or more spinels.

As mentioned above, the threshold between lighter and darker samples was determined by trial and error to create Figure 11. However, once the threshold was selected, the points were sorted into two categories objectively, and visually, there seems to be no data point that is mis-classified. In conclusion, there appears to be a mechanism that influences plasma formation and makes the plasma more suitable either when the samples are completely clear of particles, or sufficiently darkened by particles.
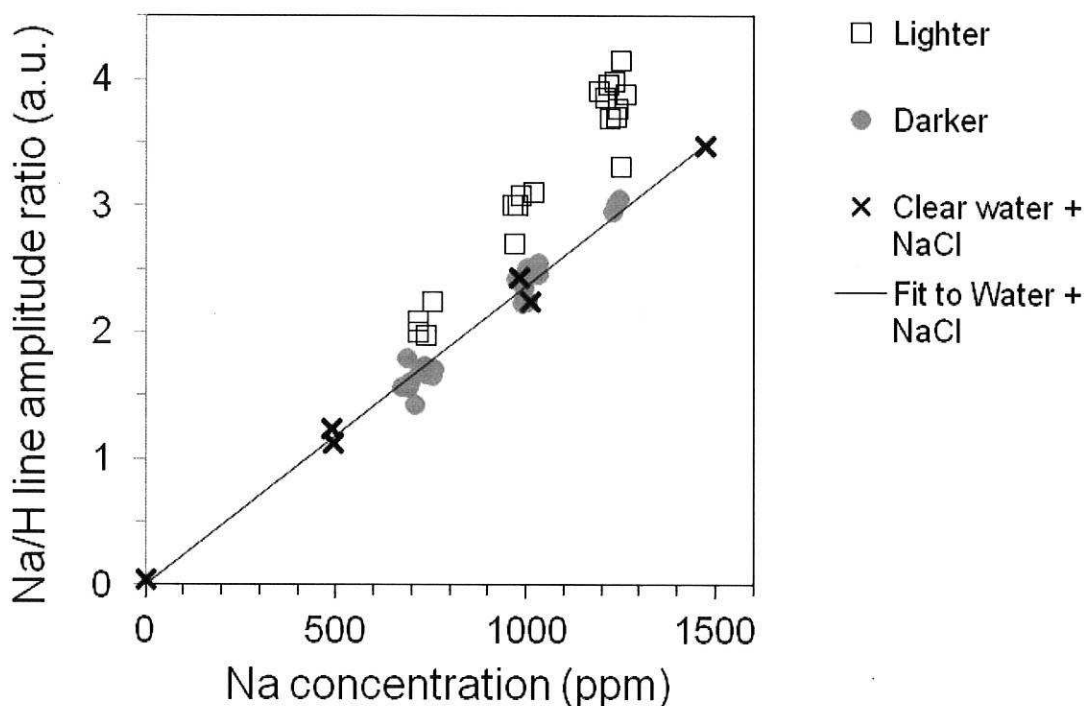

Figure 11. Normalized Na line amplitude ratio for 6 samples of NaCl aqueous solutions (X symbols) and 40 simulated process water samples of light (open squares), medium and dark colour (solid dots) as a function of Na concentration. The solid line is a linear least squares fit to the water + NaCl samples.

AEL vs. CNRL calibrations revisited

Another observation can be drawn from Figure 11. As discussed earlier in this report, the AEL measurements of elemental concentrations could be off by some systematic

amount because the AEL and CNRL measurements differed systematically. The Na concentration of the clear water samples, on the other hand, is precisely known because it was obtained from weighted NaCl additions to deionised water. If the effect of colour shown in Figure 11 is really the same phenomenon as what is observed in the model system in Figure 7, then the AEL measurements of Na concentration are valid (and the CNRL measurements must be rejected) because the darker samples and the clear water samples are on the same line. One possible explanation of the bias between AEL and CNRL is the possible aging of the solution. It is important to note that the solutions were analyzed by AEL several months after CNRL analyzed them. Therefore, if the samples aged, the measurements made at AEL would be closer to those made by LIBS.

Multiple linear correlation

In a previous section, it was shown that samples which had a N 746.9 line amplitude above a certain threshold were darker and had a good correlation between the Na/H amplitude ratio and Na concentration. The data also shows that all of the following emission lines correlate with each other: N 746.9, H_β, H_γ, O 747.7. Under the assumption that colour changes laser penetration depth and plasma temperature, these correlations are not surprising. Of these four lines, the O 747.7 line cannot be completely separated from the Al 747.3 line, so these two lines interfere with each other and should be rejected. (A different spectrometer could be used to resolve them if there were a need to do so.) This leaves only N and H lines. Various multiple least squares fit between the Na concentration and the Na, N, and H line intensities were tried. The best empirical fit was obtained using the Na 589 line and the product of the Na 589 and H_β lines from the Spex spectrometer (Figure 12). The rms residual is 30 ppm, which corresponds to a 3% error on an average Na concentration of 1000 ppm. This meets the project goals of 5% error.
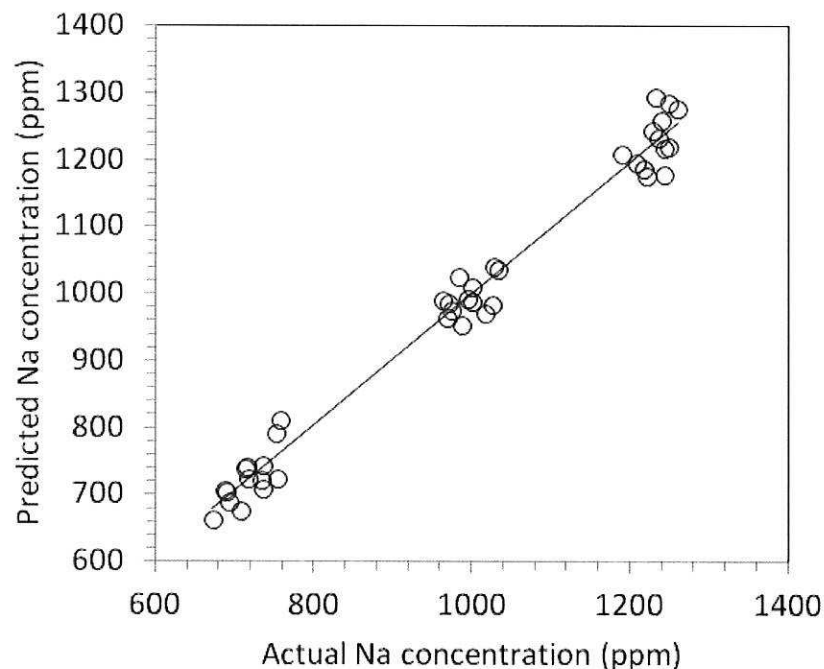

Figure 12. Best multiple least squares fit of emission lines to the Na concentration in 42 simulated process water samples.

Why would the product of these two lines enter the best fit correlation? Obviously, the Na line amplitude must enter the correlation with Na concentration. Previously, in this report, it was argued that colour affected temperature and line amplitude, and that H, N, and O line amplitude increased with temperature. However, temperature increases almost all line amplitudes, including the Na line amplitude. So we can expect a cross-correlation between Na and H or N line amplitudes. Therefore, it makes sense that the product of Na and H line amplitudes enters the correlation. Also, this line of argumentation predicts that the fitted coefficient to the product should be negative (a higher temperature causes a larger amplitude in Na, so the fit must subtract some of the Na x H product from the Na line amplitude), and the fitted coefficient is indeed negative.

Initially, in this report, it was argued that the spectra should be normalized by (divided by) the H line to take into account experimental factors such as variations in the amount of light collected because of possible fluctuations in the position of the plasma or other experimental factors. It now seems that these factors are secondary. The division by the H line amplitude did seem to improve the fits we obtained. For small variations, $1/x + \Delta x = -(1/x) \Delta x$. So for small variations on line amplitudes, dividing or multiplying by the H line amplitude should produce equally good results. So dividing by the H line amplitude did produce an improvement. However, the variations in H line amplitude are not small and we now find that using the product of the two lines provides greater improvements in the fit to Na concentration.

Measurement of Ca, Mg, K

The range on concentrations for Ca, Mg, and K in the simulated process water samples was rather small and did not allow making robust calibrations. Also, measuring the concentration of these elements was secondary to measuring the Na concentration. Nevertheless, it was possible to obtain empirical correlations between line amplitudes and the solute concentration as measured by AEL. This is shown in Figure 13. The residual is of the order of a few ppm for each element.
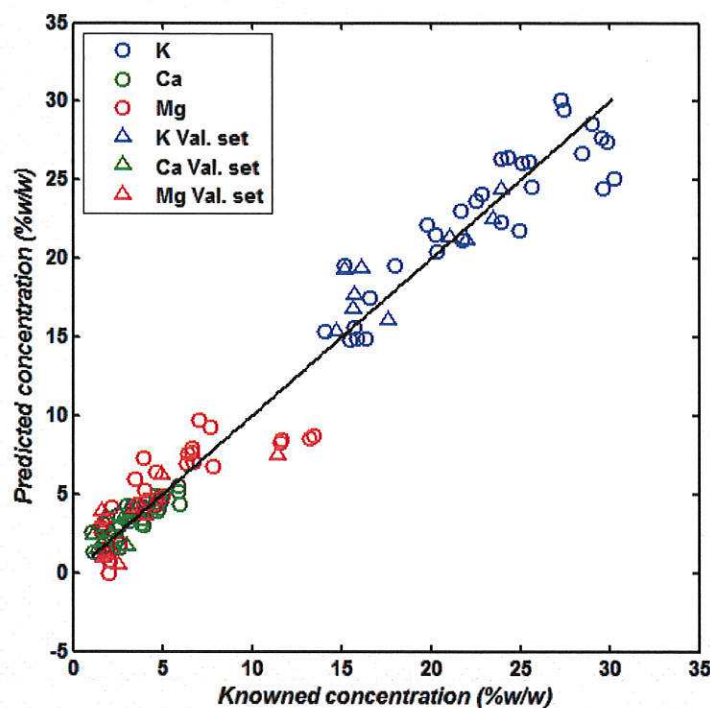
Figure 13. Predicted vs. known concentration of Ca, Mg, and K in simulated process water samples.

Non-soluble elements

Previously to this work, it was determined that the four elements of interest are present not only in solution, but also in solid form in clay and sand particles.[1] Table 6 shows the mean concentration and the concentration range for 140 samples of solids filtered out of recycled water. The table also shows for reference the expected concentration range of these four elements in process water. The solids in recycled water are essentially the same solids as those contained in process water, although variations are possible. (The original work compared the solid and solute concentrations in recycled water for both.)

Table 6. Elemental concentration means and ranges in solids from recycled water and comparison to solute concentration in process water.

Element	Concentration in Solids (wt ppm)	Concentration in Process Water (wt ppm)
Na	630 (100 - 2800)	750 - 2000
Mg	970 (100 - 4100)	0 - 20 (200 max)
Ca	970 (100 - 5000)	0 - 20 (100 max)
K	5940 (300 - 13300)	20 - 200

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[1] Dean Wallace, private communication.

Table 6 shows that the concentration of Na is of the same order of magnitude in particles and water, and the concentration of the other 3 elements in solids largely exceeds the concentration in process water. Earlier in this report, it was observed that the spinel particles always contributed to the LIBS line amplitudes. Therefore we must assume that clay or sand particles contribute too. However, and this is critical, we do not know to what extent the solid particles contribute to the plasma. Does the LIBS plasma contain mostly dissolved or solid species, or similar proportions of both?

The results obtained in the previous section indicate that the addition of up to 10 % drop water to the simulated process water and the lesser amount of filtration darkened the samples and made the measurements on simulated process water agree better with the measurement on clear water. This effect was apparently more important than any contribution the solid particles might have had to the line amplitudes. This indicates that the contribution of solute elements to the LIBS measurement is much larger than the contribution of solid particles.

Measurements on process water

Samples of real (not simulated) process water were obtained. By the time they arrived, most of the solids and bitumen had sedimented. The samples were let to rest a few weeks. Then, some of the water was skimmed using a pipette. This water was then analyzed using the LIBS system and the method of standard additions. Solids were also collected from the bottom of the containers and dried. The dried solids were then added to the skimmed water until they reached a concentration of 1%. This suspension was then analyzed again using LIBS and the standard addition method. The results are shown in Figure 14.
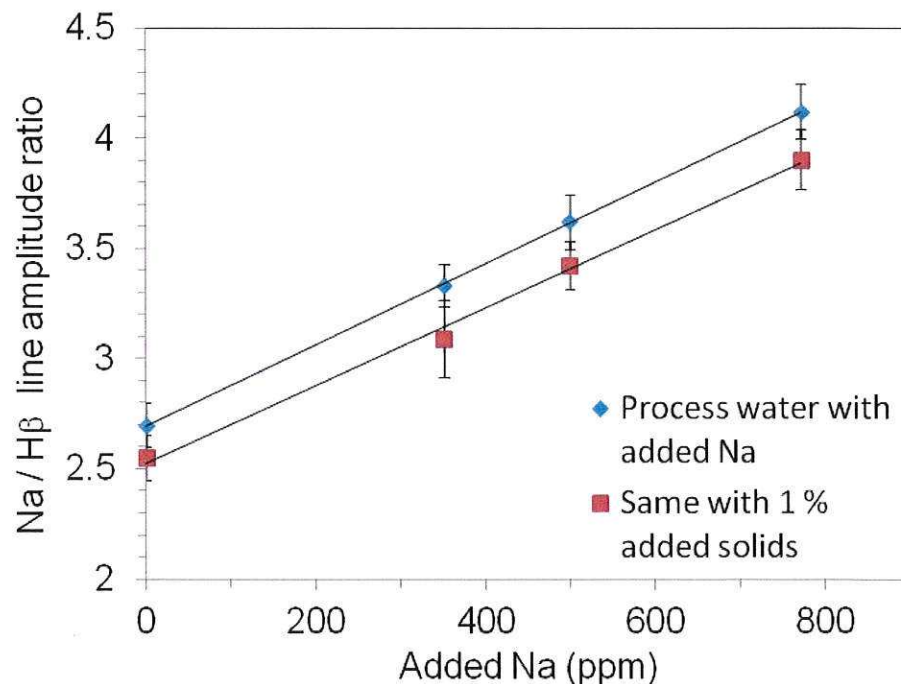

Figure 14. Na / H_β line amplitude ratio vs standard additions of Na for decanted process water (blue diamonds) and the same water with 1% addition of dried solids (red squares).

The actual Na concentration can be obtained by extrapolating the linear least squares fit of the Na / H_β line amplitude ratio to the x-axis. The Na concentration obtained is 1460 for the process water and 1433 ppm for the same water with 1% addition of solids. These results are nearly identical. The solid addition changed the water colour from light to dark. According to what was found on the spinel model system and according to the simulated process water samples, we expect the Na / H_β ratio should be the same or lower for the darker samples, as observed in Figure 14.

More importantly, the previous section raised the question as to whether the solids contributed significantly to the measured concentration. Figure 14 shows that their effect is negligible on the measurement of Na concentration.

Measurements on water + interburden

Samples of interburden were obtained. They were mixed with de-ionized water and analyzed with the LIBS system. Figure 15 shows some of the individual spectra that were obtained. The majority of the recorded spectra were from the water, possibly with a small contribution from small particles. However, it appears that large particles were often hit by the laser, and this resulted in spectra that were noticeably different and characteristic of the composition of the particle. Three spectra were selected in Figure 15. The bottom spectrum is from a water sample and is representative of the soluble elements. The middle spectrum is Al-rich and could be representative of an alumina particle. The top spectrum is very rich and shows that the particle contained Ti, Mg, Al, and Ca. If larger particles are present in the water to be analyzed, the effect of particles could be rejected by rejecting the spectra with such intense emission lines.
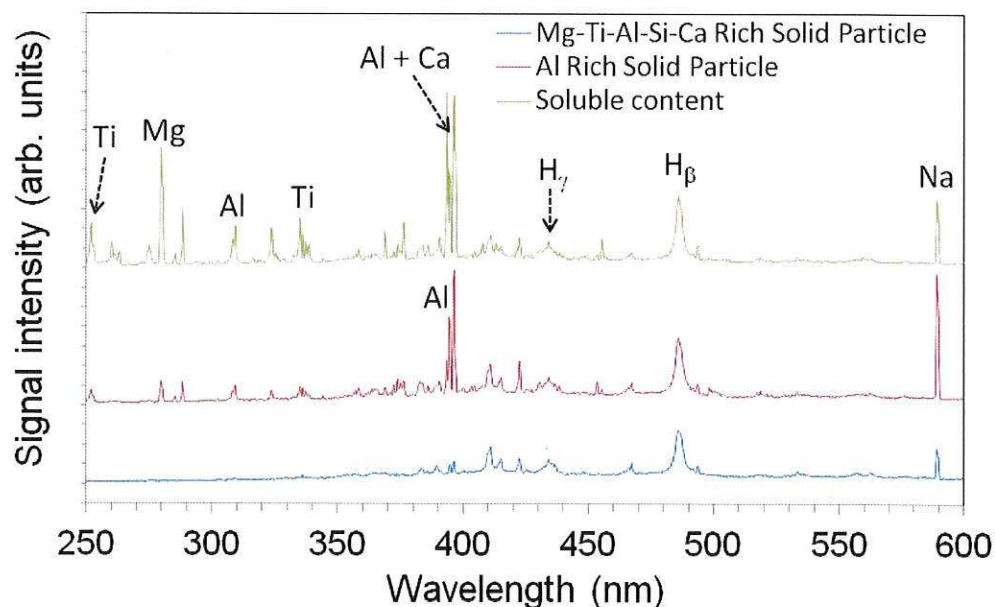

Figure 15. Three spectra from water mixed with interburden showing the effect of different interburden particles on the spectra. Top: Spectrum from a solid particle rich in Ti, Mg, Al, and Ca. Middle: Spectrum from an Al-rich particle. Bottom: Spectrum free of large particles. The three spectra have an arbitrary vertical offset to improve clarity.

5. Conclusion

The objective of this project is to measure the concentration of four elements, Na, Mg, Ca, and K, in solution in process water before bitumen is extracted by froth floatation at CNRL. Of these four elements, it is far more important to obtain the concentration of sodium. CNRL plans to install a filter that will remove all particles from the process water, leaving water that is crystal clear. Using such celar, particle-free water samples, this project did not encounter any difficulty in measuring the Na concentration (or the concentration of other elements).

It is not certain that the filter to be isntalled will function properly. Simulated process water filtered to various degrees contained particles in suspension and were coloured. This project showed that, if the filter does not work properly, the LIBS measurement will be more difficult, but can still be done. Specifically, we found that:

In a model system consisting of de-ionized water in which NaCl is dissolved and insoluble spinel ($MgAl_2O_4$) particles are suspended:

- The ratio Na/H line amplitude is the same for a given sodium concentration provided that the water is either free of particles or the particle concentration exceeds 0.5%.

- The spinels always contribute to the LIBS plasma because Al and Mg emission lines were always detected.

In simulated process water samples:

- The line amplitude ratio Na/H is the same as for a solution of deionized water and NaCl of the same Na concentration provided that the samples were dark enough, or the amplitude of the N, O, or H lines exceeded some threshold.

- A multilinear regression allowed to measure Na concentration for all samples with a precision of ±3%.

- It was also possible to measure the concentration of the other three elements (Ca, Mg, K) to within ± a few ppm but we had a limited spread on concentrations, which reduces our confidence in this result.

- Although we expect that the solid particles in suspension contribute to the LIBS spectrum, they do not contribute significantly to the amplitude of the Na line, and therefore do not affect the measurement.

In real process water that has been decanted

- We were able to measure Na concentration by the method of standard additions.

- Adding 1% of dried solids to form a suspension did not affect the measurement.

- If there were hydrocarbons left in solution in the decanted water, then they did not appear to affect the measurements.

In a suspension of interburden in water:

- Large particles of interburden have sudden contribution to individual spectra and these sudden contributions can be easily identified. Therefore, to measure the concentration of elements in solution, it would be easy to reject those events and keep only the spectra characteristic of the elements in solution.

Therefore, if the filter to be installed online does not function optimally and provides water that contains some amount of particles, our work shows that the measurements are likely going to be more robust if the particle concentration exceeds some minimum amount. However, even if it does not exceed this minimum concentration, it is likely that we can make a correction to the measured spectra that would compensate for the effect the particles have on plasma formation. The current hypothesis, which has been verified to some degree, is that particles change the penetration depth of the laser beam. The measurement of a nitrogen, hydrogen or possibly oxygen line can be used to build an empirical correction. Such a correction has allowed us to measure Na concentration with a precision of ±3%, which exceeds the goal of measuring with a precision of ±5%.

This project considered the effect of different solid particles. Therefore, the results of this project can probably be applied to other locations in the oil sand extraction process. However, the effect of bitumen was not considered because bitumen is extremely difficult to handle. For example, it will clog circulation systems at room temperature.