

Next Generation Spectrophotometer System for Enhanced In-process Pu Monitoring of Effluent Waste Streams – 17268

Jean Plummer*, David Immel*, Robert Lascola*, Patrick O'Rourke*
Edward Kyser III *, Christopher Loyal **

* Savannah River National Laboratory (SRNL)

** Savannah River Nuclear Solutions (SRNS)

ABSTRACT

The Next Generation Spectrophotometer (NGS) system is an in-process monitoring system developed by SRNL to determine Pu concentration in nuclear processing streams at the Savannah River Site (SRS). Development of the NGS system began from a need to replace aged Pu monitoring equipment whose measurement uncertainty greatly reduced process throughput. The NGS system implements absorption spectroscopy technology to determine total Pu concentration and Pu valence state distributions by measuring the light absorbance of a solution. The NGS system was completed and installed in the later part of 2016. It provides an excellent example of process intensification, i.e. replacement of aged systems with smarter, more accurate and operationally efficient systems.

This paper will detail the capabilities of the NGS system, its application in the nuclear processing stream, and operational challenges working with Pu solutions. Discussion will include the development of the virtual instrument which negates the intrinsic differences between actual instruments and implements a technique that performs continuous intensity and waveform calibration. Other notable features discussed are the development of a new modeling application method which applies custom models based on the current operating region of the process and the ability to perform in-field calibrations using NIST-traceable standards. Lastly, the benefits encapsulated in the final system including the significant improvement in measurement certainty, process intensification efficiencies, and the ease of adaptability of this system for use with other actinide and chemical measurement applications will be discussed.

INTRODUCTION

The NGS system was developed to support Pu recovery from spent nuclear fuel and other sources at the SRS HB-Line nuclear material processing facility, Fig. 1. The chemical separation process in use in HB-Line results in the production of purified plutonium oxide, Fig. 2. Process monitoring of the Pu concentration during the process is performed to protect criticality limits in the receiving tanks and to maximize the efficiency of Pu recovery.



Fig. 1. SRS HB-Line Nuclear Processing Facility

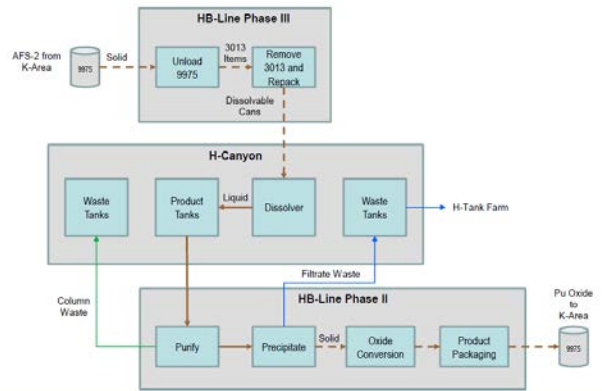


Fig. 2. HB-Line Plutonium Oxide Production Overview

Pu purification is achieved with ion exchange columns, Fig. 3. The source material is adjusted to a high concentration of nitric acid and pumped through the column where the Pu preferentially attaches to the column resin and contaminants are flushed away. Once the resin is saturated, low molar nitric acid is pushed through the column in the opposite direction, causing the Pu to elute (“wash off”) the resin. The NGS system monitors the Pu concentration in the anion column effluent (“discharge”) flow cell and sends results to the facility Distributed Control System (DCS). Based on these results, a downstream valve is adjusted to direct process solution to a collection tank when concentration is high and to the waste tank when concentration is low. As a secondary safety measure, Pu concentration is measured in the waste stream (“raffinate”) to protect criticality limits for the receiving tank.

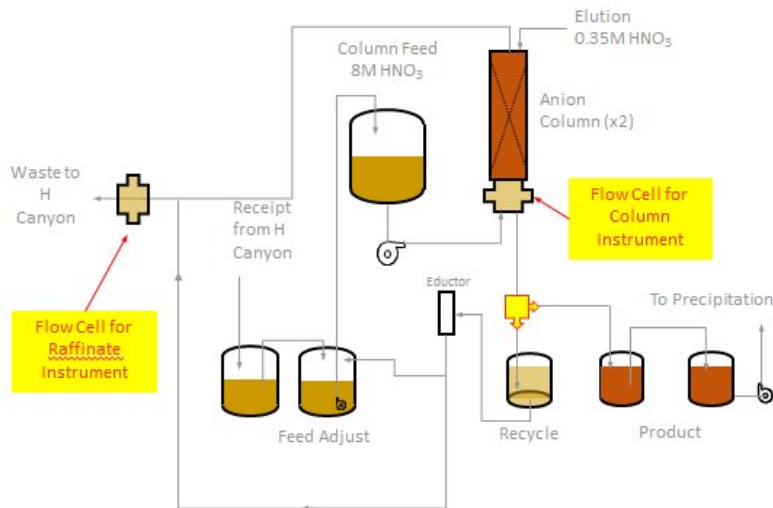


Fig. 3. HB-Line Pu Extraction Process

Measurement Considerations

Pu measurements in HB-Line are performed using absorption spectrometry. The measurement system shines a fiber optic delivered light through a process flow cell and the resultant light spectrum is read by the instrument. The amount of light absorbed by the process solution at specified wavelengths is used to determine Pu concentration. The light absorbance is dependent on the Pu valence state, nitric acid concentration and Pu concentration [1]. An example of the effect of nitric acid concentration on the color of the primary Pu valence state (Pu⁴⁺) is shown in Fig. 4.

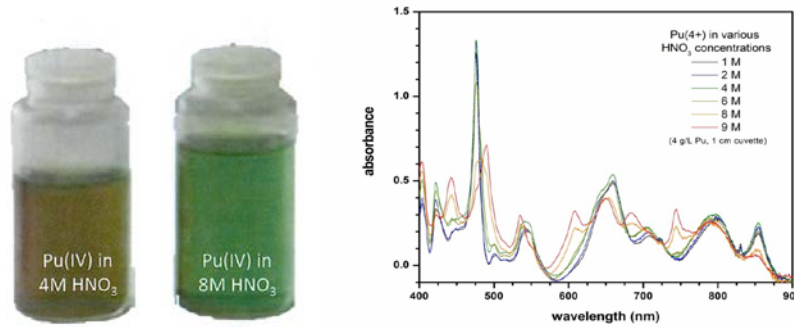


Fig. 4. Effect of nitric acid concentration on process solution color (left) and absorbance read by instrument (right)

Other Pu valence states can appear through a disproportionation reaction which occurs at certain process conditions, Eq 1. These also result in absorbance spectrum changes, Fig. 5. Solution acidity and Pu valence state must be characterized for the process and addressed in the final calculation models developed for the system.

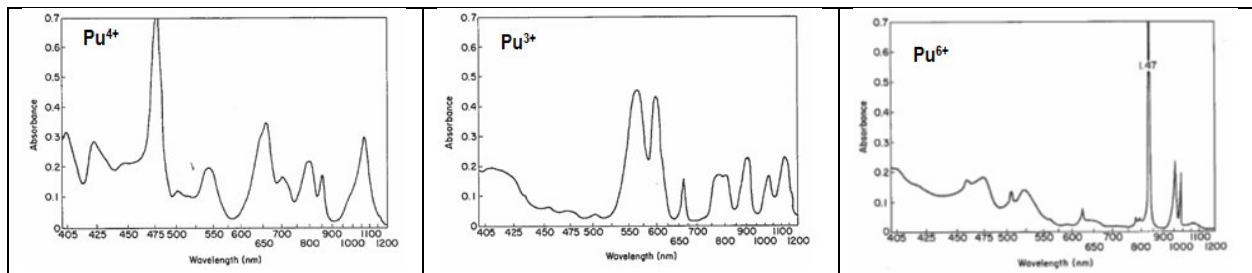
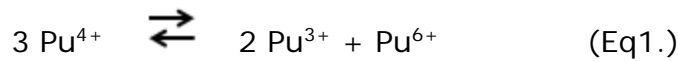


Fig. 5. NGS spectrometer based system reads absorption across a range of wavelengths allowing for Pu valence states (shown above) to be identified to calculate a more accurate Total Pu value

DESCRIPTION

System Goals

The primary goal for the NGS system was to gain accuracy and replication of results across the entire range of the elution process. Very high measurement errors were

calculated for the existing colorimeters based on uncertainty associated with nitric acid concentration (~15%) and bias associated with plutonium oxidation state disproportionation (-35%). These errors greatly reduced process throughput by requiring very conservative operating set points to preserve criticality safety.

Secondary goals included the desire to standardize instrumentation across several facilities and laboratories to simplify and reduce maintenance and recalibration efforts. Concerns relating to the colorimeter systems included the need for frequent maintenance, especially the replacement of rapidly aging lamps. Additionally, because standards cannot be introduced into the field process flow cell to perform calibrations, planned outages were required to remove instrumentation from the field to be recalibrated in a laboratory.

Process Intensification

The NGS system is a highly successful application and demonstration of process intensification (PI). Ponce-Ortega et al. [2] defined PI as an activity characterized by five principles—reduced size of equipment, increased throughput of process, reduced equipment holdup or inventory, reduced usage of utilities and raw materials, and, increased efficiency of process equipment. Actualization of many of these principles with dramatic results will be seen as the development and resulting NGS system is discussed in this paper.

Development Overview

The new NGS system has been designed around the use of the spectrophotometer instrument which allows for the measurement of absorption over a wide range of wavelengths. Instrument selection was followed by the development of the novel concept of an ideal virtual instrument which negates intrinsic instrument differences through a specific instrument configuration and data processing algorithms. Additional process improvements were made during the development of the field deployable system and the development of a new model application approach. These activities are described in the following sections.

New Instrument Basis: Colorimeters versus Spectrophotometers

The NGS system was developed to replace three existing Pu monitoring systems based on the colorimeter instrument which allows for the measurement of light absorbance at a single wavelength (with measurement of a reference signal at second wavelength), Fig. 6. This scheme was suitable for the original measurement scope, in which Pu would be measured under conditions where only the Pu⁴⁺ valence state would appear. However, there is no single sample wavelength that can be measured which allows for consistent Pu readings in the new mission where a larger set of variations and Pu valence states are

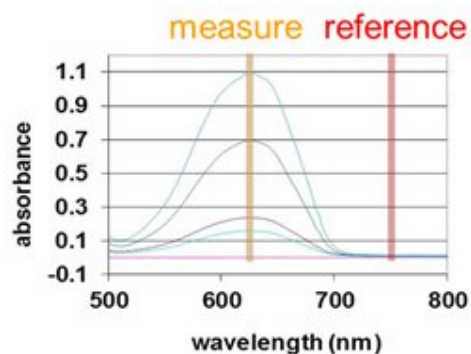


Fig. 6. Generic colorimeter application where absorbance at one wavelength is measured

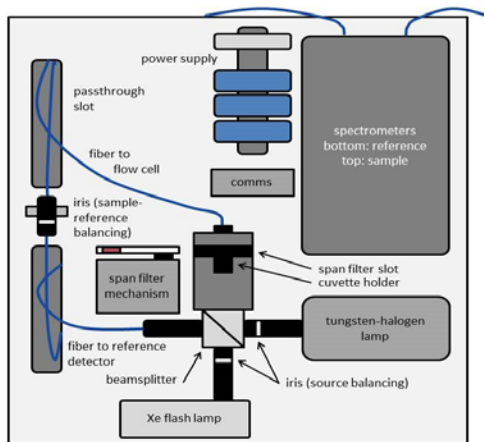
expected.

The new NGS systems are based on a spectrophotometer instrument which reads the entire absorbance spectrum (wavelengths 360-920nm), providing the required amount of data and allowing for the individual identification of the Pu oxidation states. The NGS control software acquires the data and runs the calculations which interpret the absorbance spectra to provide estimates of the total Pu concentration and the distribution between oxidation states. The instrument uncertainty depends on the process conditions, but is less than 5% in any of these cases, which is much less than the values obtained with the colorimeters.

The 'Ideal Virtual Instrument'

The NGS ideal virtual instrument is a system of hardware and algorithms developed by SRNL that negate the intrinsic differences between actual instruments. After investigating and testing multiple potential instrumentation and configuration solutions to provide reproducible results and to support instrumentation standardization, the concept of the virtual instrument emerged. In theory, absorbance spectral data are intrinsic to a material and should be independent of the particular spectrophotometer used for the measurement. In practice, each instrument through the manufacturing process and factors such as aging and environment has minor differences that cause it to deviate from the ideal instrument.

The NGS instrumentation configuration includes a sample and a reference diode array spectrometer, a xenon lamp and a tungsten lamp, Fig. 7. The light outputs of a tungsten lamp and a xenon arc lamp are combined into a single source then split for use as the light source on both the sample and reference spectrometer paths.



Further corrections are made to account for nonlinear (non-ideal) response of the spectrometers to light intensity from phenomena such as detector dark current and instrument stray light.

Fig. 7. NGS Instrument Shelf Schematic Diagram

Wavelength correction is based on the sharp line atomic emissions from the xenon lamp which are continually present in each instrument's collected spectra, Fig. 8. The true wavelengths of these peaks are known physical constants. The peak wavelengths in the acquired spectrum are determined automatically and corrections are calculated by comparison of the apparent and known values. The corrections occur in real time and are made for each spectrum that is collected.

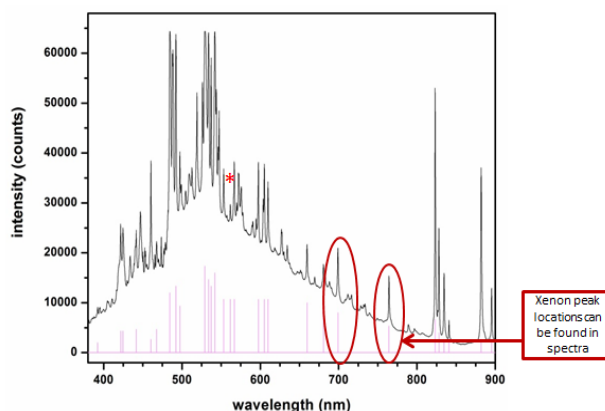


Fig. 8. Xenon peaks present in acquired spectra are used for waveform correction

The calculation of an absorbance spectrum requires the two spectrometers to have the same response to intensity variations and must compare that response for the same wavelengths. The intensity corrections described above satisfy the first condition. The second condition is not satisfied by comparing the two diode arrays on a pixel-by-pixel basis since the two instruments will not have the same calibrations. The problem is solved by creating a virtual instrument, in which each spectrum is interpolated to a fixed set of virtual wavelengths. For example, in the NGS instrument, the wavelengths are spaced by 0.2 nm (400 nm, 400.2 nm, 400.4 nm, etc.). The accuracy of the interpolated values is determined by the accuracy of the correction to the xenon lamp reference lines. This accuracy is typically 0.02 nm, which is much smaller than the width of the features in the absorption spectrum and is sufficient for Pu measurements.

The intensity and wavelength corrections that are done to allow the reference and sample spectrometers to be compared in a single NGS unit also assure that separate NGS units will give identical measurements within the accuracy of the corrections. Thus, the corrections and interpolations serve to create an 'ideal virtual instrument' that standardizes light absorbance measurements and, in this application, subsequent measurements of plutonium.

M&O Focused System Design

Three NGS systems were built and mounted in a single cabinet, Fig. 9, to replace three individual colorimeter systems. The hardware and software program are identical for the three systems providing standardization across the three monitored locations. The NGS systems are highly configurable through the use of software startup files which contain system configuration and operational settings read into memory upon program startup. Additionally, model files developed for each application are loaded into memory during startup. Changes made to configuration settings and model selections while using the NGS program are simultaneously written to memory and saved to the associated configuration file on disk to be available during the next startup.



Fig. 9 – HB-Line NGS Cabinet with close up of NGS #1 and shared monitor

Each NGS system consists of an instrument shelf, Fig. 10, an instrument display panel, a computer, and an Opto 22 I/O system. The replaced colorimeter systems included cabinet indicators displaying current Pu concentration and had a limited user interface which made troubleshooting difficult. The NGS system not only provides an expanded front instrument display panel but as shown in Fig.9, includes a shared monitor for accessing the control program’s extensive graphical user interface. The instrument display panel is designed so that users typically seated in other locations in the control room (~ 20 feet away) can easily determine the status of each spectrophotometer system.

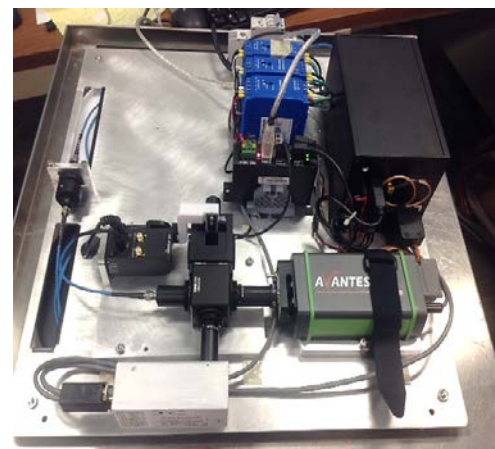


Fig. 10 NGS Instrument Shelf

The NGS computers are mounted behind the monitor and the I/O is mounted on two swing doors located in the rear of the cabinet, as shown in Figs. 11 & 12. The NGS computers share a single touchscreen monitor and keyboard to save space in the control room. A keypad is available on the upper right side of the monitor that allows the user to select which NGS system to display on the monitor, Fig. 13. Also shown in the figure is the cabinet’s fiber optic connection box designed to ease NGS installation by simply disconnecting existing in process fiber optic lines from the colorimeter then reconnecting them to the NGS terminal box. Because the NGS cabinet hosts three individual systems and includes space for a fourth system,

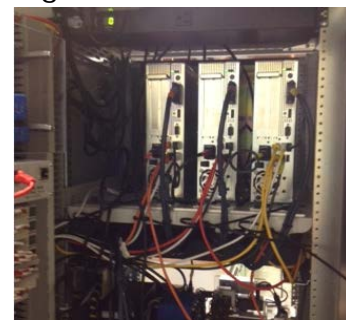


Fig. 11. NGS computers mounted behind monitor

the internal wiring is color coded to easily identify which cabinet components belong to which system.



Fig. 12. Cabinet digital I/O system

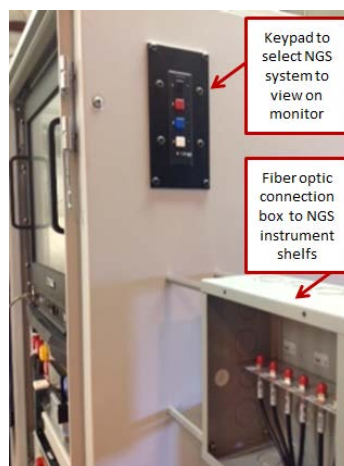


Fig. 13 Cabinet monitor keypad selector and fiber optic junction box

NGS Instrument Software

A new instrument control software program was written in order to take full advantage of the developments in hardware and data analysis associated with the spectrophotometers. In addition to performing the enhanced data acquisition, processing and interpretation, the program includes the following major benefits and features:

- Improved process awareness
- Extensive system health diagnostics
- In field calibration using NIST-traceable standards
- Modeling subsystem implementing novel method of analysis and model application

Improved Process Awareness

The NGS main display allows for easy viewing of the current Pu concentration, any disproportionation occurring in the process, and a summary of the health of the system, Fig. 14. Extensive diagnostics includes process information such as whether the flow cell contains bubbles or striations, instrument health such as acceptable lamp intensity, and quality checks on acquired spectrophotometer data.

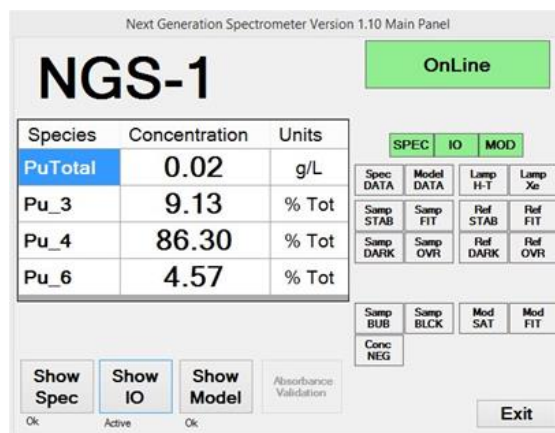


Fig. 14. NGS control program Main display

The NGS software provides a host of process information and configuration displays not available on the previous system. Software displays include viewing of the spectrometer and lamp status and settings, current sample and reference spectra both in raw data and transformed forms, process settings and current status of algorithm applications. Several of these displays are shown in Fig.15.

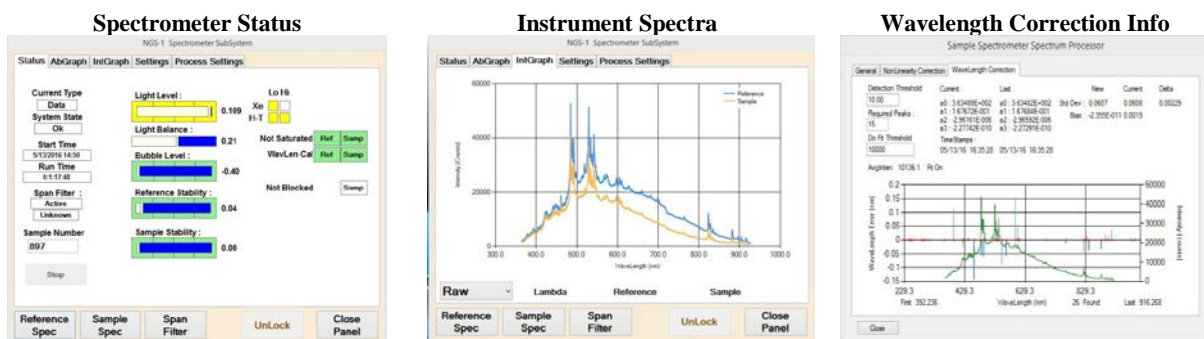


Fig. 15. Examples of NGS control program information and configuration displays

The NGS software additionally archives all collected raw data, final calculated and reported results, and associated system health and diagnostic values. This data can be retrieved and replayed offline to better understand the process and the effects of different software settings on the final results. Operations personnel have taken advantage of this feature since installation to replay and evaluate in depth the elution process steps and other process activities such as system flushing.

In Field Calibration

Implementation of the NGS technologies has resulted in a system whose instrument performance can be confirmed in the field with NIST-traceable absorbance standards. Testing has confirmed that different instruments will produce identical absorbance spectra within the uncertainty of the standard, Fig. 16. The ability to perform in field calibrations is a significant operational efficiency as previously the colorimeters had to be returned annually to the laboratory for calibration. Additionally, these annual calibrations resulted in new instrument spans which prompted a significant effort to update a number of field documents.

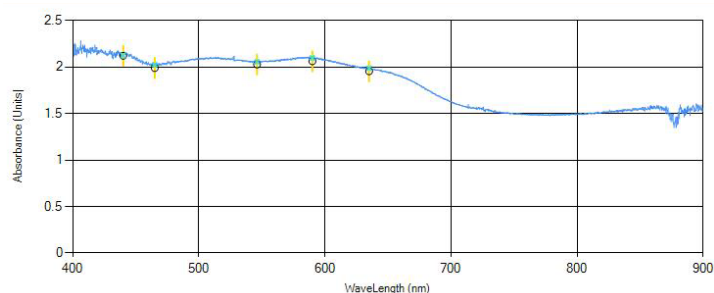


Fig. 16 - Absorbance readings of five NIST standards on three different instruments

The NGS control software enables and guides the user in performing the field calibration through the use of the Absorption Validation Panel, Fig. 17. NIST wavelength standards are inserted into a span filter which is easily accessible by sliding out the instrument shelf. Once the standard is inserted, the user can instruct the program to read, process and evaluate the reading of the NIST standard.

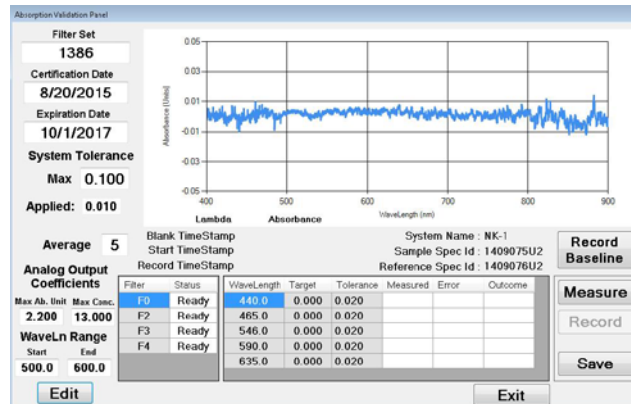


Fig. 17. Absorption Validation Panel used to perform in field calibration with NIST standards

Modeling Subsystem

A key component to the reuse of the NGS system across multiple processes is the implementation of the modeling subsystem in the control. A custom modeling solution can be developed for a specific process then loaded into the NGS software using the Model Main form with no recompilation needed, Fig. 18. The NGS software passes corrected absorbance spectrum to the currently loaded model then receives and displays the data object returned from the model. This data is also forwarded to the NGS Main Display where it is displayed and the first data element is sent to the DCS system and displayed on the instrument control panel. For HB-Line the first data element is PuTotal.

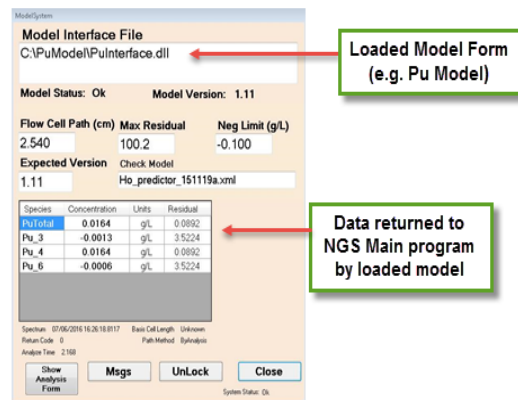
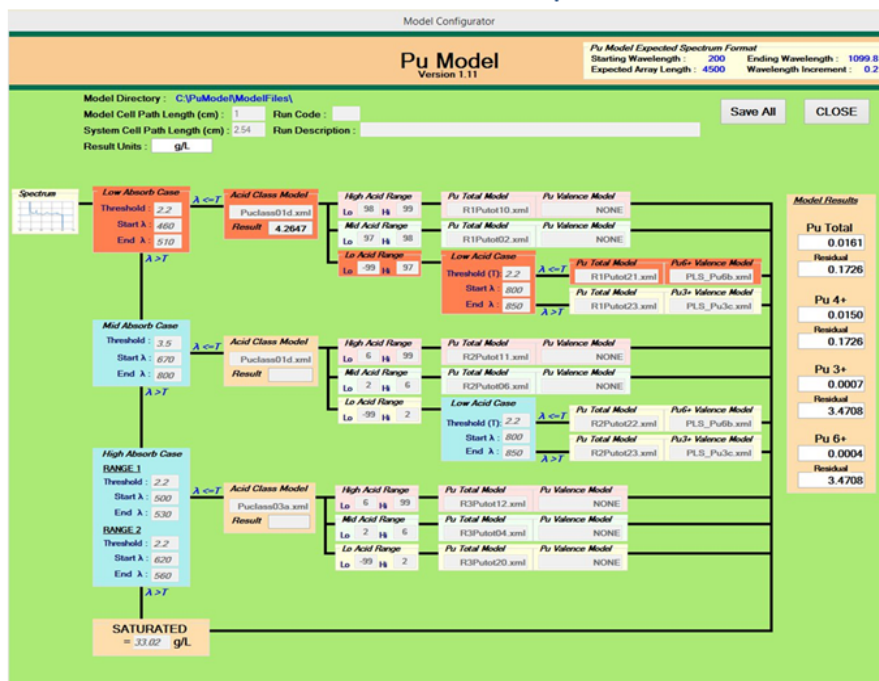
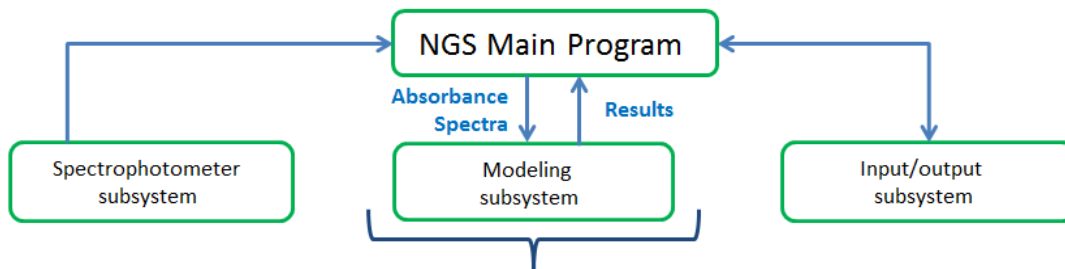


Fig. 18.- Main Model subsystem display

Novel Model Implementation Method

The Pu model developed for HB-Line implements a novel approach developed by SRNL which applies custom models based on the current operating region of the process, Fig. 19. Each corrected absorption spectrum passed to the model is classified into one of eleven regions based on Pu concentration, solution acidity, and disproportionation. Based on the classification, models developed specifically for the current operating environment are applied to determine acidity, Pu⁴⁺ concentration and, if the potential for disproportionation exists, a Pu Valence model to determine Pu³⁺ and Pu⁶⁺ concentrations.

This classification scheme allows for the development of simpler models that are more accurate than could be obtained from one complex model applied over the entire range of process conditions. Individual models developed for a classification path can be loaded and unloaded on this form with no need to modify or recompile the field software. The classification path of the current spectrum is highlighted in a coral color on the Pu Model form for easy user identification. This is an interesting feature that allows the viewer to “watch” the process Pu concentration and acidity progress through the elution cycle.



Modeling Software

- Classification of spectrum by :
 - absorbance range (low, mid, high)
 - acid range (low, medium, high)
- Total Pu model applied based on classification
- Pu Valence model applied, if potential for disproportionation
- Improved accuracy by applying classification specific models

Fig. 19. Pu Model developed for HB-Line process

DISCUSSION

Process Improvements

Accuracy

The NGS instrument uncertainty is less than 5% over the entire elution process which is a dramatic improvement over the previous colorimeter system whose calculated measurement uncertainty was ~15% with a bias associated with Pu disproportionation of -35%. High colorimeter measurement uncertainties resulted in very conservative operating set points negatively impacting Pu recovery during the process. The NGS significantly improved accuracy has notably increased the efficiency of Pu recovery during elution achieving benefits of increased process throughput, reduction of effluent directed and collected in the waste stream, reduced required 'raw material' and reduced usage of utilities.

The NGS system accuracy has been gained through a series of process intensification improvements to include better instrumentation, development of the Virtual Instrument methodology, greater process awareness and control through new software, and the implementation of a novel modeling scheme. NGS instrument improvements enable the ability to measure absorbance over the entire visible spectrum, rather than at just one wavelength as is done with the colorimeters. The extra data obtained allows for identification of Pu valence states and the development of more accurate and sophisticated statistical models to better determine concentration. Additionally, xenon peaks in acquired data can now be identified to perform waveform standardization to a common basis. The Virtual Instrument method calculates wavelength accuracy to better than one-fifth of the optical resolution of the spectrometers, and corrects intensity to better than 1 part in 1000 [1]. Control software has enabled in-depth observation and fine-tuning of system performance and enhanced monitoring of system health. And lastly, measurement accuracy is enhanced by the development and implementation of a modeling scheme which classifies spectra according to absorbance and acidity, then applies models optimized for that region.

Operational and Maintenance Efficiencies

The system improvements enhancing accuracy have also enabled significant operational and maintenance efficiencies:

- In field calibration and performance checks. The NGS system has automated, continuous control of wavelength and intensity calibrations, which are confirmed through the measurement of NIST traceable absorbance standards. The absorbance standards are readily measured in the field. We have demonstrated that accurate measurement of the standards translates to accurate Pu measurements, thus precluding any need to relocate the instruments to the laboratory to measure Pu standards directly. The in-field performance checks can be performed in about 30 minutes per instrument using stepwise procedures versus the previous laboratory check which required several weeks to complete.

- Improved Process Awareness. The NGS system software provides for easy 'viewing' of the elution process, has implemented extensive system and process diagnostics and includes the ability to store and replay raw data and final reported results. This has led to a much better understanding and monitoring of the process and has led to several unanticipated benefits. Operation organizations have found the additional information useful when performing maintenance and troubleshooting elsewhere in the process and have incorporated the use of the NGS system during these activities. For instance, NGS diagnostics includes the ability to determine if the monitored flow cell has bubbles or striations which is very useful information when performing certain flushing operations.
- Reduced lamp maintenance. Lamp intensity degradation from rapid lamp aging and a high sensitivity of the colorimeter instrument to the changing lamp output had led to monthly field calibrations and frequent lamp replacement. The monthly calibrations required significant commitment of worker resources and dedicated down time to flush the system and re-zero instruments. The NGS virtual instrument compensates for lamp aging and intensity changes between lamp replacements and the NGS software now provides diagnostics to immediately alert the user to any lamp malfunction. Additionally, the instrument was designed to facilitate easy access to the lamps for replacement in the field using stepwise procedures.
- Improved Instrument Standardization. The improved self-calibration and performance checks not only assure more consistent performance for a single instrument, but also reduce variation between different instruments. This allows Pu calibrations developed in the laboratory to be directly deployed on multiple field instruments without a need to mathematically characterize and correct for the intrinsic differences between instruments. This removes a significant source of error and allows for easy model updating in the field.
- Simplified Model Development. Classification of spectra by absorbance and acidity allows for the development of simpler models addressing the conditions of the current process versus development of one complex model to cover all conditions over the entire process. Maintenance of multi variable models is often a significant effort in the implementation of absorbance spectroscopy systems; the tiered approach of classification and quantitation simplifies maintenance and improves robustness. Additionally, the software was designed to allow for easy loading of new models in the field without requiring recompilation of the software.

Reusability and Opportunities

The NGS was designed to be highly configurable to support reuse of the system and the goal of instrumentation standardization across SRS facilities and laboratories. New concentration models to measure other material species, such as uranium, can be developed and loaded into the current system without modification to the NGS hardware and software. The NGS system is not only useful within the DOE complex

but has applicability to a number of industries that monitor chemical manufacturing processes including pharmaceuticals, pulp/paper and food providing a more accurate, reliable and easier to maintain system.

CONCLUSIONS

SRNL has developed, built and installed a spectrophotometer based system to replace colorimeter based systems for monitoring plutonium in effluent streams at several locations in HB-Line. Technologies developed and implemented in the NGS system have significantly increased measurement certainty and simplified operations and maintenance activities. The instrument is self-referencing for both wavelength and intensity measurements and the performance is confirmed with NIST-traceable absorbance standards. The system derives additional accuracy through a spectral classification scheme based on solution acidity and absorbance.

The NGS developed and installed system has been highly successful in not only meeting the primary and secondary system goals but has developed and implemented novel instrumentation and software techniques. While there has been substantial investment in development, the resultant system will be reused as a solution at several SRS locations. The NGS system is highly configurable and applicable not only to other process systems at SRS and throughout the DOE complex, but to the many industries which monitor chemical processes.

REFERENCES

- [1] "Spectrophotometers for Plutonium Monitoring in HB-Line", R.J.Lascola, P.E.O'Rourke, E.A.Kyser, D.M.Immel, J.Plummer, E.V.Evans, SRNL-STI-2015-00454, Revision 0 January 29,2016
- [2] Ponce-Ortega JM, Al-Thubaiti MM, El-Halwagi MM (2012) Process intensification: new understanding and systematic approach. Chem Eng Process 53:63–75. doi:10.1016/j.cep. 2011.12.010