SAND2017-5427C

Exploration and Analysis of Historical Pu(IV) Oxalate Precipitation

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First off…

I am a Statistician with chemistry data and 1602 pages of documentation.

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…not a chemist.

Background

- R&D program to study continuous precipitation of Pu(IV) Oxalate was established by Rockwell Hanford Operations at the U.S. DOE Hanford Site during the 1980s.
- Goal: provide technical support to a new line being added to the PUREX facility to convert plutonium nitrate solution to plutonium oxide (PuO_2) through intermediate synthesis of plutonium (IV) oxalate, $Pu(C_2O_4)_2 \cdot 6H_2O$, in a continuous precipitation process.

How do process parameters affect plutonium oxalate and the resulting product characteristics?

The data

Factors/Precipitation Conditions	Responses
Residence time (min)	Nucleation Population Density (#/(ml-μm))
Precipitation slurry suspension density (g $Pu(C_2O_4)_2/\ell$)	Growth Rate (μm/s)
Agitator speed (rpm)	Nucleation Rate (#/(ml-s))
$C_2O_4^{=}/Pu^{+4}$ (RMR)	Average Size (μm)
NO_3^{-}/Pu^{+4} (MR)	Dominant Size (μm)
$C_2O_4^{=}/NO_3^{-}$ (MR)	Total # Agglomerates (#/ml)
Ionic strength of the precipitation slurry (Molar)	Soluble Pu (Molar)
Precipitation temperature ($°C$)	Calculated Equilibrium Solubility (Molar)
	Surface Area (m^2/g)
	Crystal Group

Responses obtained from:

- Precipitation kinetic analysis
- Particle-size distributions
- Surface-area measurements
- SEM photomicrographs
- Pu(IV) oxalate equilibrium solubility

The data

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- SEM photomicrographs
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The experimental design

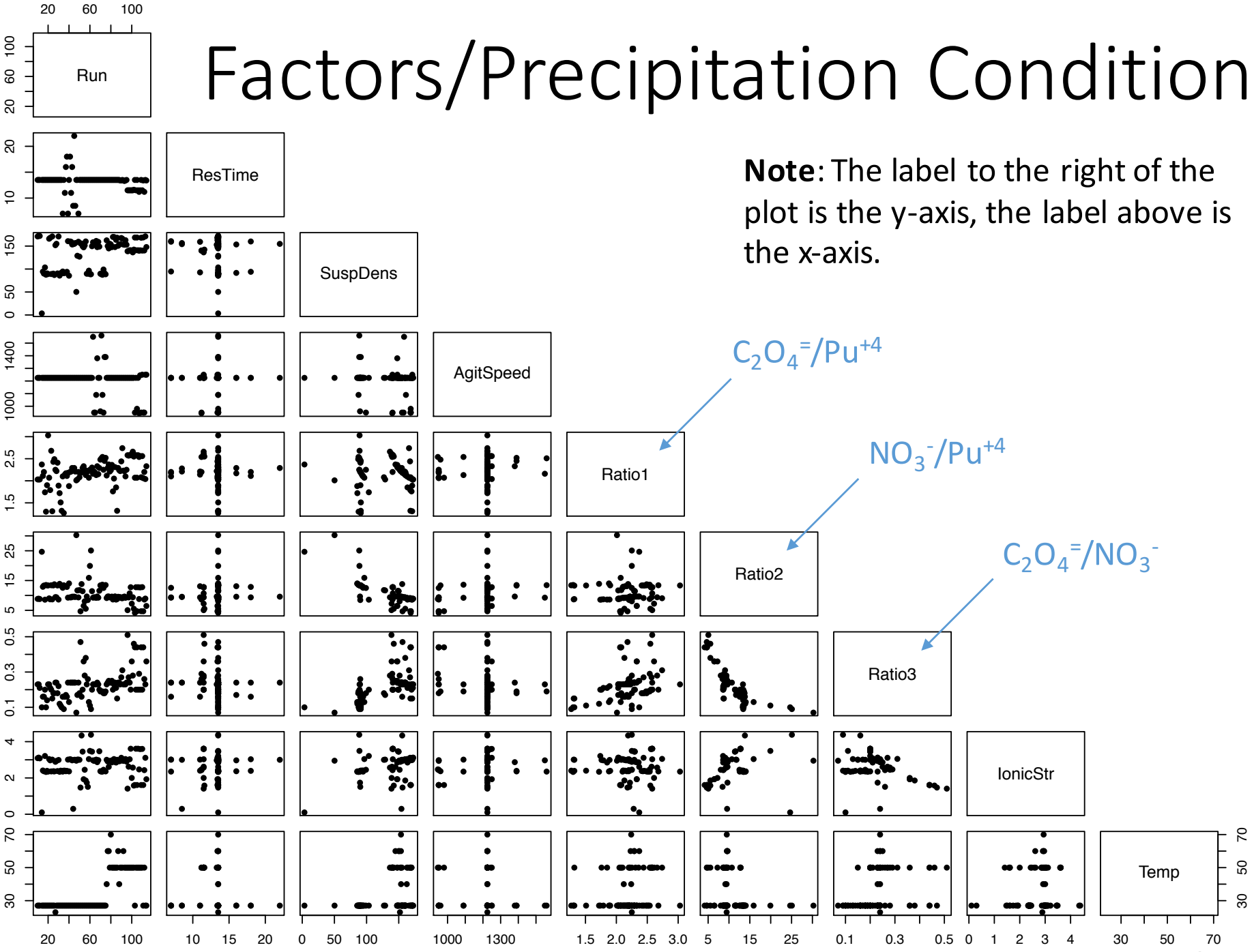
- Approach: Up-to-date examination of experimental results followed by careful selection of the next set of process conditions for study.
  - Experimental runs were repeated as necessary for periodic confirmation/clarification
    - 18 precipitation experiments were repeated anywhere from 1-3 times with the process conditions replicated as best possible.
    - Many of the repeated runs were performed a significant time after the original experiment

Experimental Precipitation Sub-Groups

Precipitation Cases Investigated	Suspension Density (g Pu(IV) Oxalate/ℓ)	Residence Time (min)	Oxalate/Pu RMR	Ionic Strength (M)	Temperature (°C)	Agitator Speed (RPM)
1	90	13.5	1.3 - 3.0	2.45	27°	1225
2	170	13.5	1.3 - 2.2	3.0	27°	1225
3	160	13.5	1.3 - 2.75	2.95	50°	1225
4	90	13.5	2.2	1.5 - 4.4	27°	1225
5	155	13.5	2.25	1.5 - 4.3	27°	1225
6	140	11.5	2.60	1.4 - 3.6	50°	1225
7	3.3	13.5	2.35	0.1 - 1.65	27°	1225
8	90	13.5	2.45	2.4	27°	950 - 1560
9	155	13.5	2.25	3.1	27°	950 - 1550
10	155	13.5	2.25	2.95	27° - 70°	1225
11	95	7 - 18	2.15	2.4	27°	1225
12	155	7 - 22	2.2	3.0	27°	1225
13	3 - 170	13.5	2.1	2.75	27°	1225

Shaded areas indicate the parameters that were varied for each case.

Factors/Precipitation Conditions



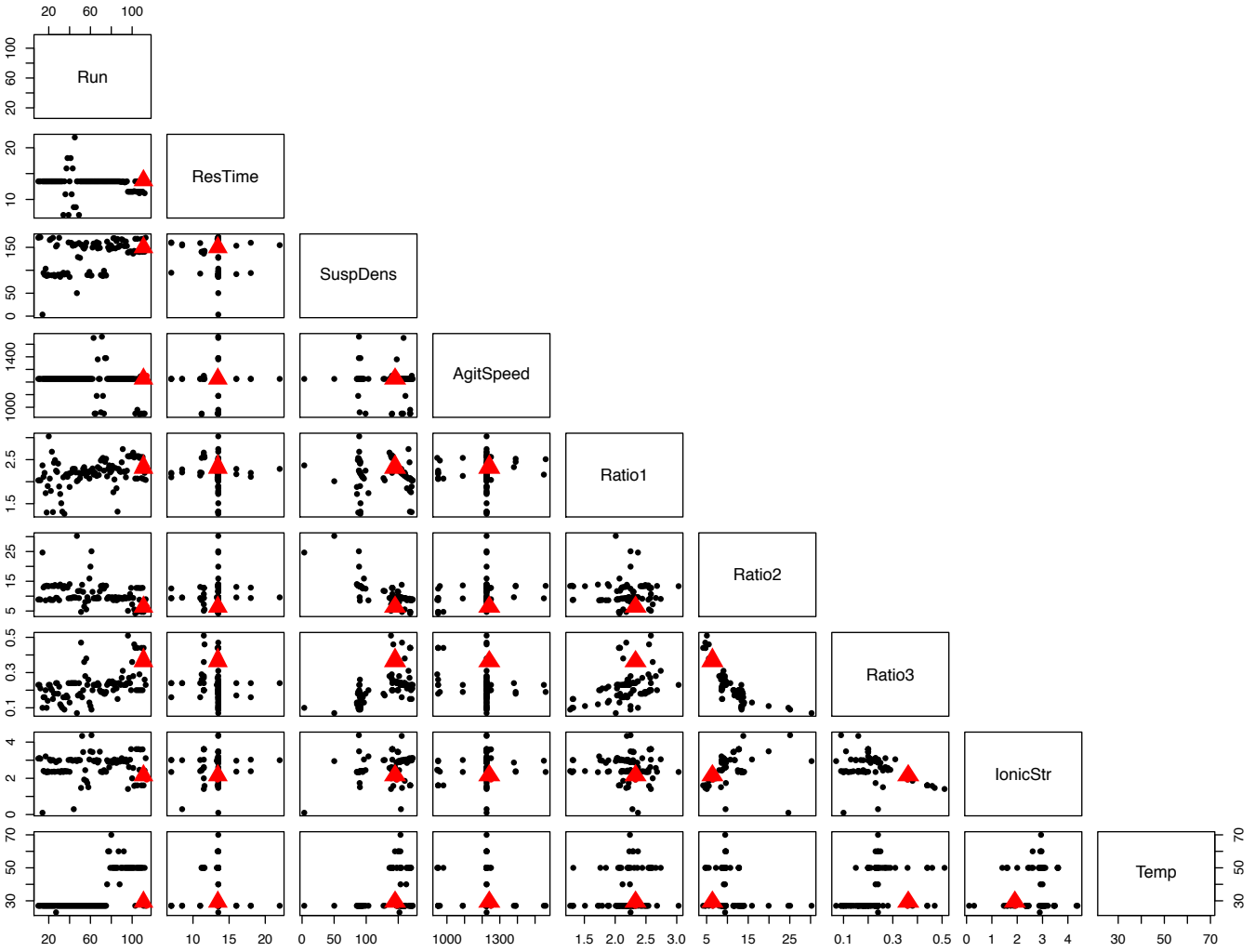
Note: The label to the right of the plot is the y-axis, the label above is the x-axis.

One run- Factors

Factors

Responses

Run	114
ResTime	13.4
SuspDens	147.9
AgitSpeed	1250
Ratio1	2.33
Ratio2	6.47
Ratio3	0.36
IonicStr	1.93
Temp	27
NuclPopDensity	1940000
GrowthRate	0.00998
NucRate	19320
AveSize	8
DomSize	24
TotAgg	15490000
SolPu	0.0001297
CalcEquil	0.0000879
SurfArea	24.2
CrystalGr	4



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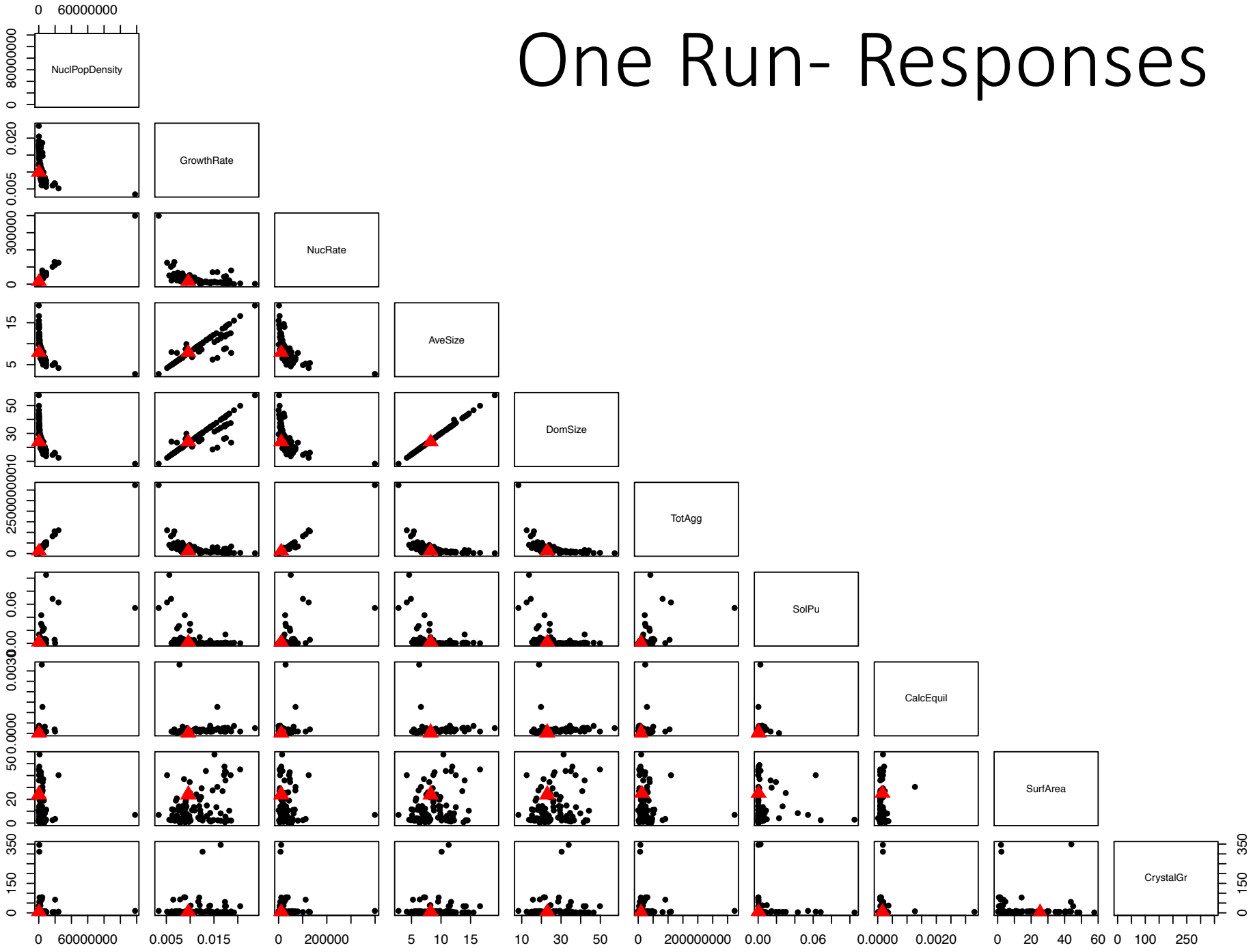
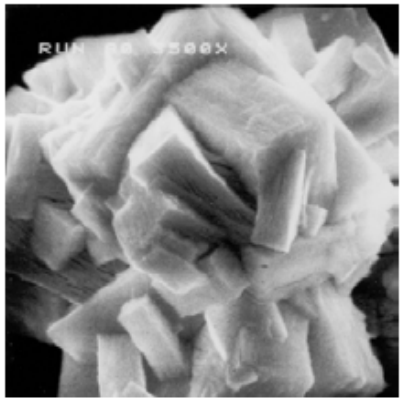
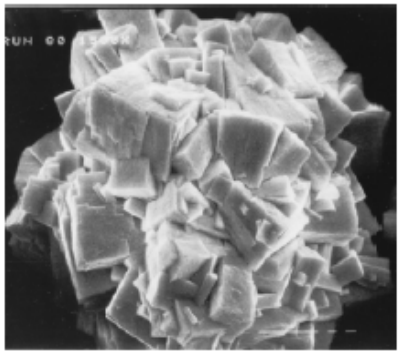
One Run- Responses

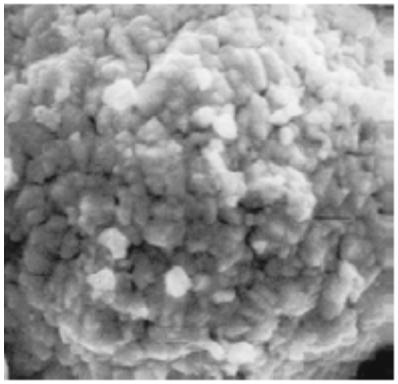


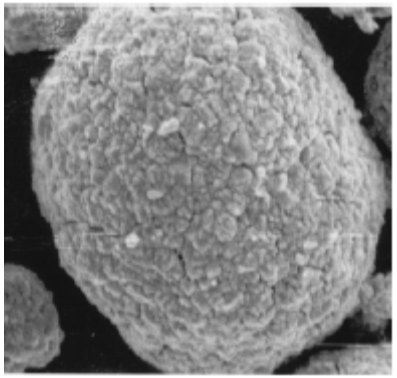
A Few Crystal Groups



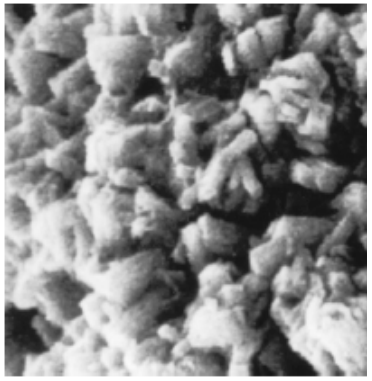


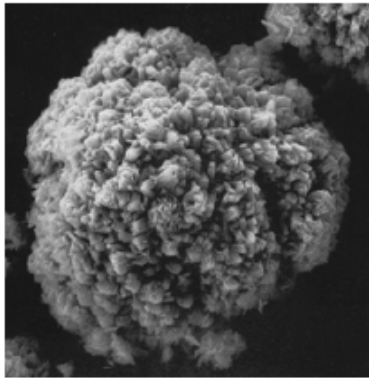
Group 2
Shape: Approx. spherical
Habit: 'Blocky'; rectangular and box-like.



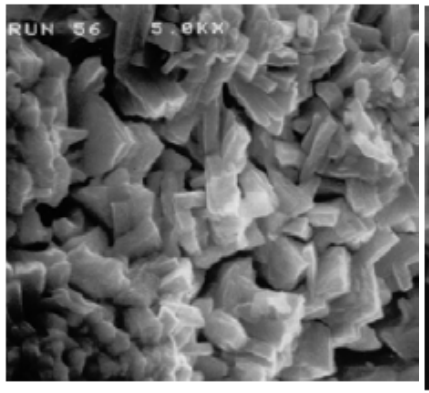


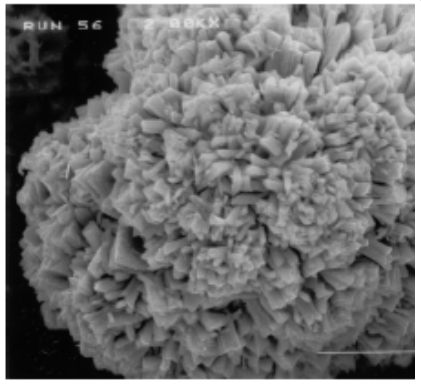
Group 4
Shape: Spherical
Habit: 'Druse', where the particle surface is covered by tiny, small crystals.



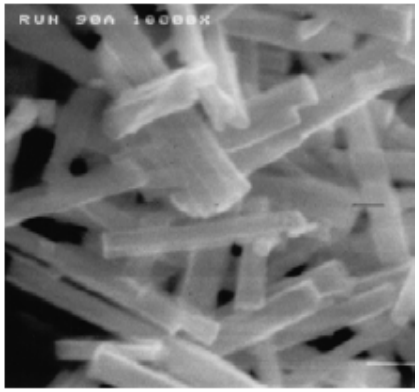


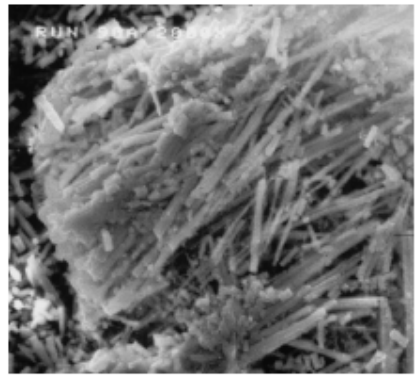
Group 6
Shape: Spherical
Habit: 'Druse', but the surface crystal Druse has more open porosity than that of Group 4.





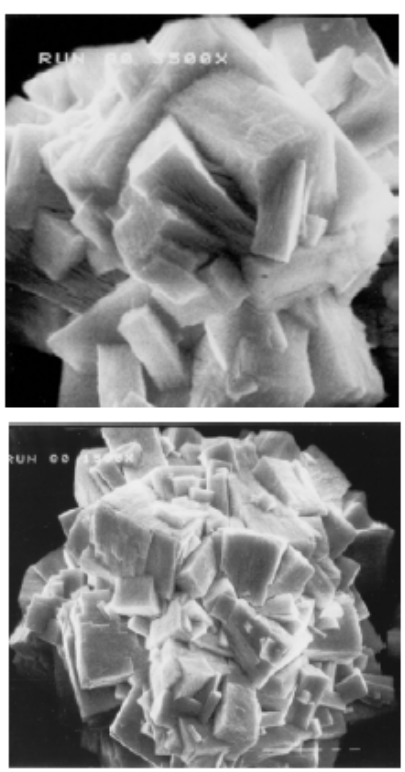
Group 8
Shape: Approx. spherical
Habit: 'Reticulated', where the crystals form net-like intergrowths of 'Blocky' type rectangular crystals.





Group 11
Shape: Primarily single crystals
Habit: 'Acicular' or 'Cubic', depending on whether the crystals resemble fine needles or small cubes, respectively. (These crystals formed during precipitator start-up and represented the temporary metastable polymorph.)

A Few Crystal Groups



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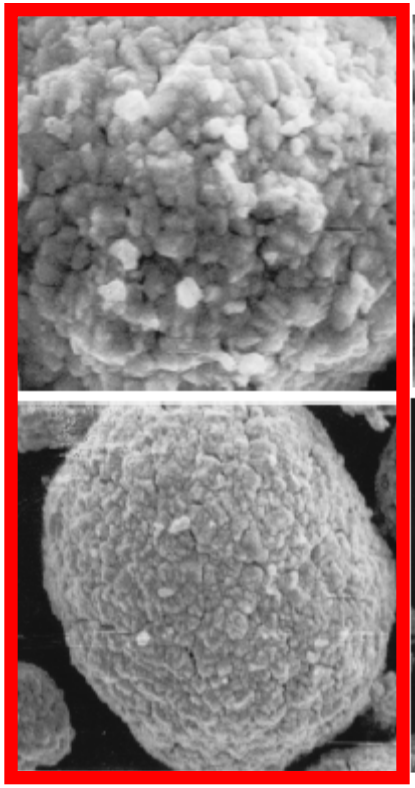

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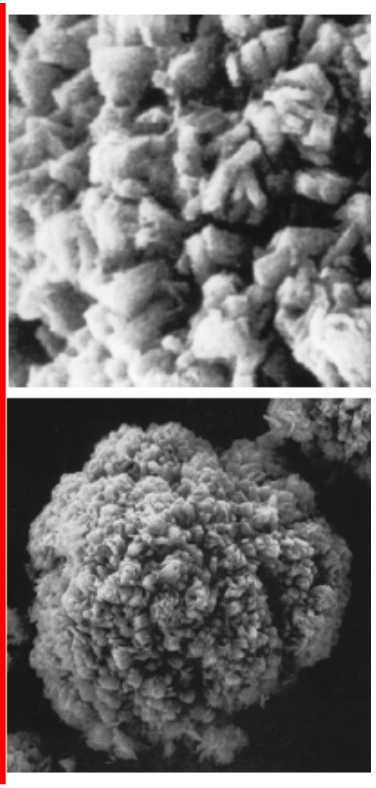

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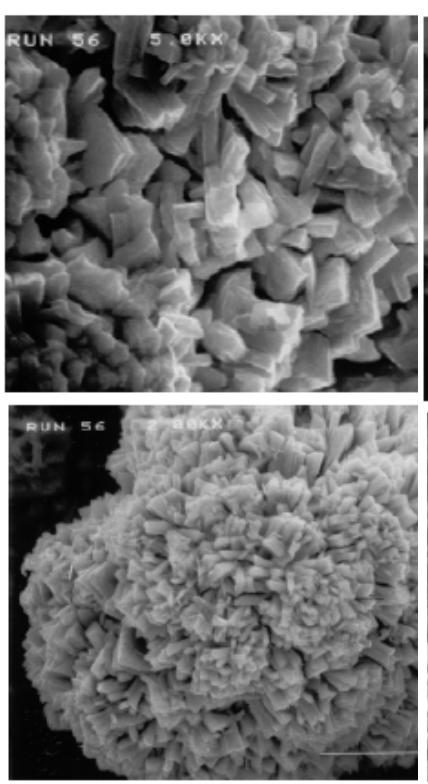

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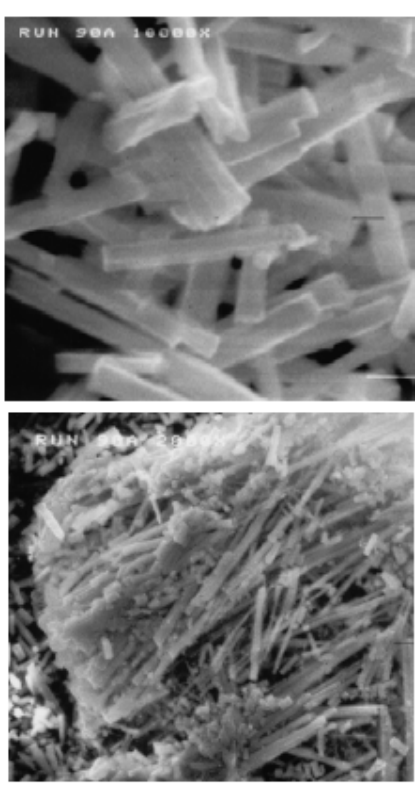

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Run 114's Crystal Group. Not all runs are characterized by just one group.

Revisiting the goal

How do process parameters affect plutonium oxalate and the resulting product characteristics?

As an addition:

Can we *predict* the various responses based on the the processing conditions?

Models

First order model ("main effects")

$$Y = \beta_0 + \beta_1 X_1 + \cdots + \beta_k X_k + \varepsilon$$

First order model with interactions

$$Y = \beta_0 + \beta_1 X_1 + \cdots + \beta_k X_k$$
$$+\beta_{1,2} X_1 X_2 + \cdots + \beta_{k-1,k} X_{k-1} X_k + \varepsilon$$

Measures of quality of fit:

R^2 = fraction of variability explained by the model

R^2_{adj} = estimate of fraction of future variability that model could explain

“All models are wrong, but some are useful.”

- George Box

Model Performance

Response	Best Model*	$R^2(R^2_{adj})$
NuclPopDensity	1st + int w/log	85% (76%)
GrowthRate	1st + int w/log	84% (74%)
NucRate	1st + int	72% (55%)
AveSize	1st + int w/log	80% (68%)
Tot#Agg	1st + int w/log	84% (75%)
SolPu	1st + int w/log	91% (86%)
CalcEquil	1st + int	98% (96%)
SurfArea	1st + int	50% (18%)

* Best $\mathbf{R^2(R^2_{adj})}$ among:

- 1st order
- 1st order w/log transform on response
- 1st order + interaction
- 1st order + interaction 1/log transform on response

Model Performance

Response	Best Model*	$R^2(R^2_{adj})$
NuclPopDensity	1^{st} + int w/log	85% (76%)
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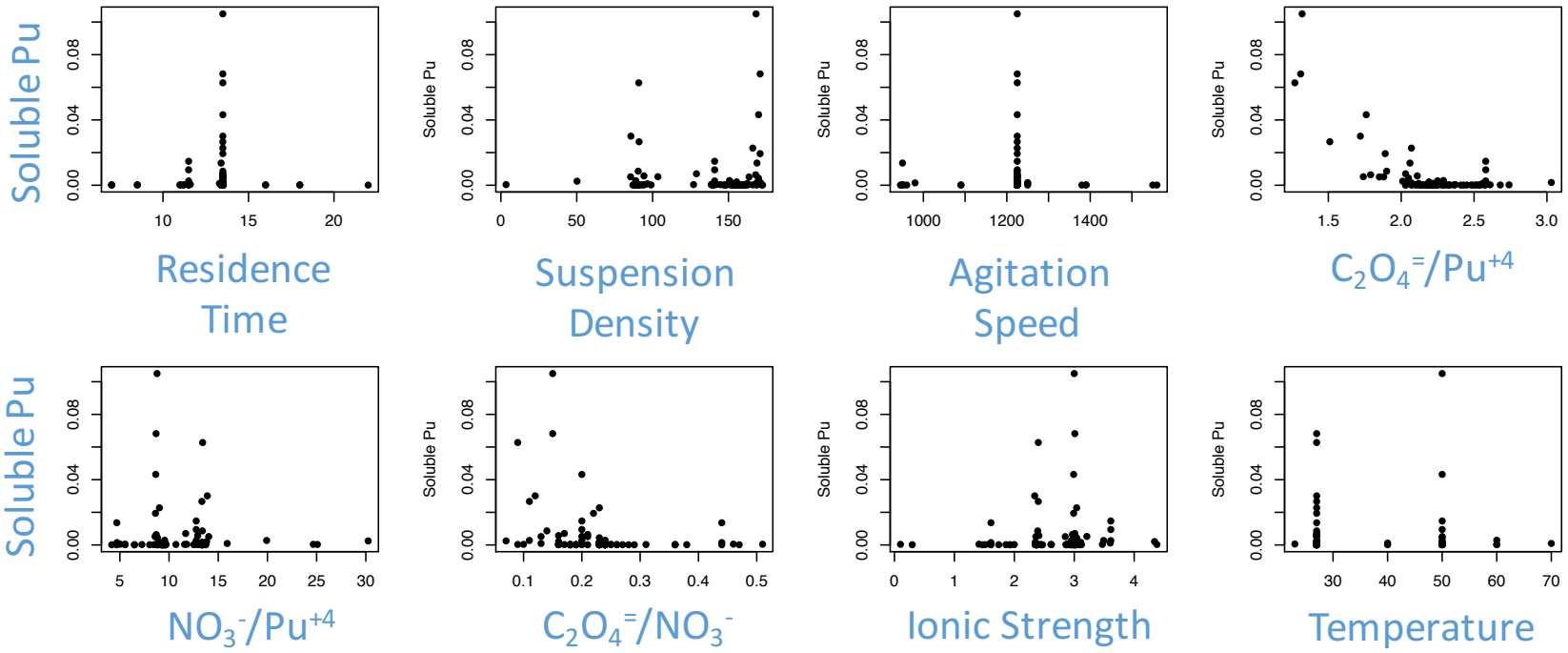
SurfArea	1^{st} + int	50% (18%)

Let's look at one response and its model…

Soluble Plutonium

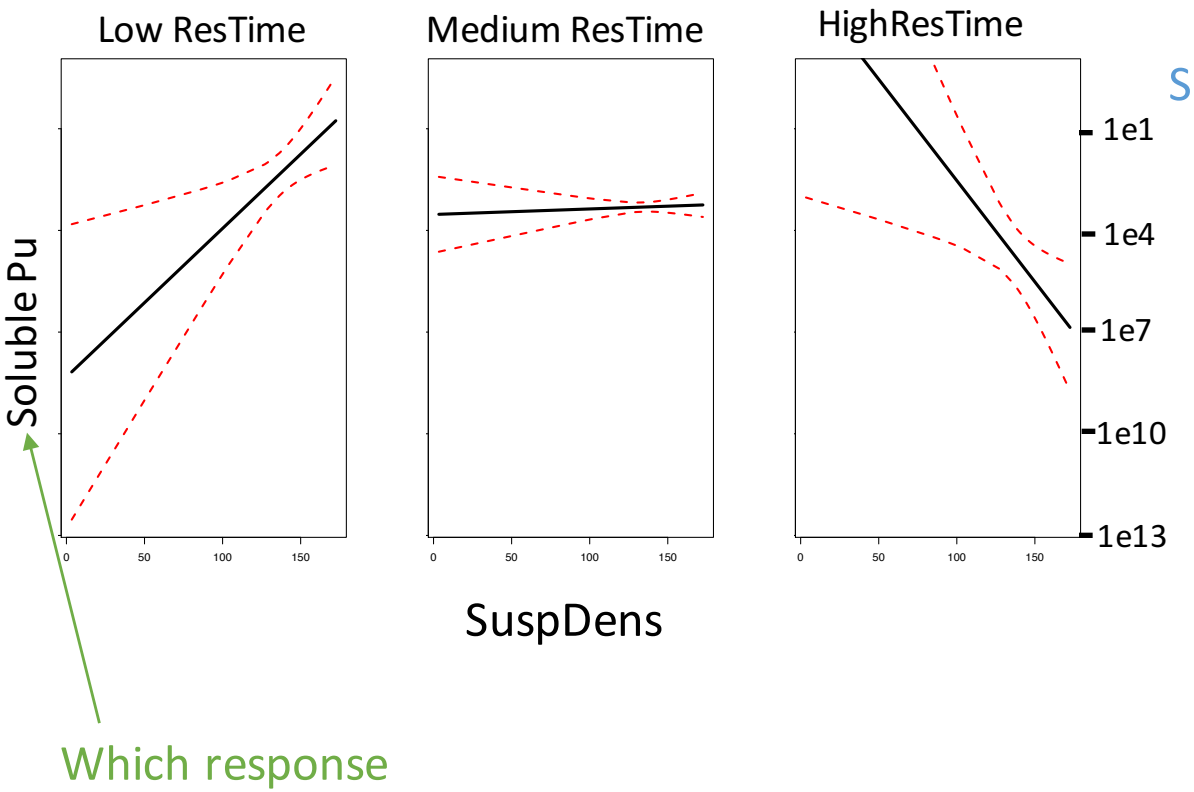
- Amount of soluble plutonium remaining in the filtrate.
- Determined by withdrawing some of the precipitator slurry with a syringe and forcing the solution through a 2-3µm filter for discharge into 2 sample vials.



Interactions: Effect Plot

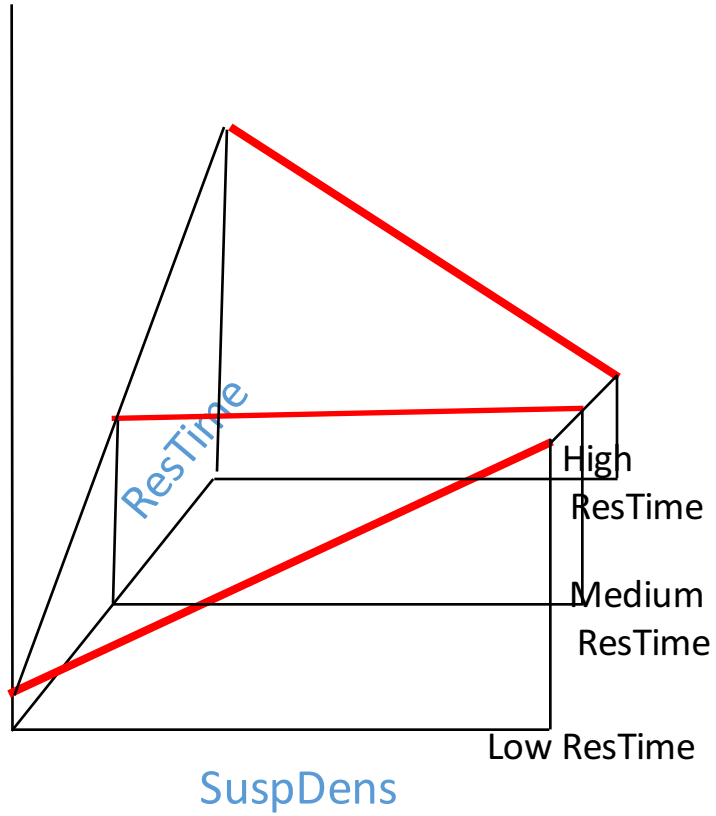
Which inputs

SuspDens*ResTime effect plot



Which response

Three panes in the plot are the three "slices" of the surface.



Soluble Plutonium Model

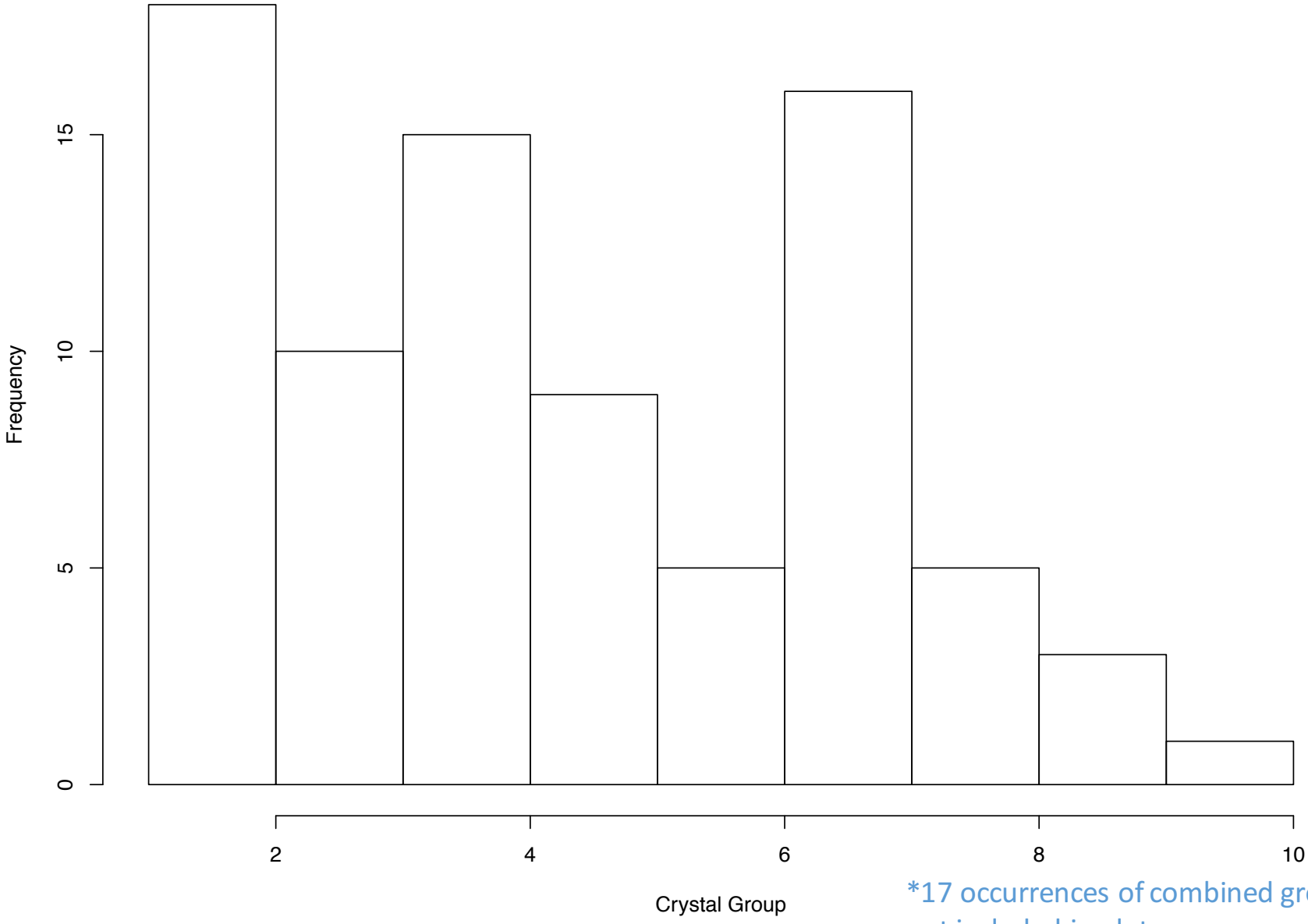
- The best model doesn't necessarily have the largest $\mathbf{R^2}$.
  - A simplified model may be more desirable for ease of interpretability and robustness.
- [More] interactions [probably] exist, but we can't estimate them well with the given data.
  - Design can be improved to cover the space.
- A more realistic model for Soluble Plutonium given the data has $\mathbf{R^2(R^2_{adj})}$ = 66% (59%).

Model Performance

Response	Best Model*	$R^2(R^2_{adj})$
NuclPopDensity	1^{st} + int w/log	85% (76%)
GrowthRate	1^{st} + int w/log	84% (74%)
NucRate	1^{st} + int	72% (55%)
AveSize	1^{st} + int w/log	80% (68%)
Tot#Agg	1^{st} + int w/log	84% (75%)
SolPu	Model building (use 1^{st} + some int)	66% (59%)
CalcEquil	1^{st} + int	98% (96%)
SurfArea	1^{st} + int	50% (18%)

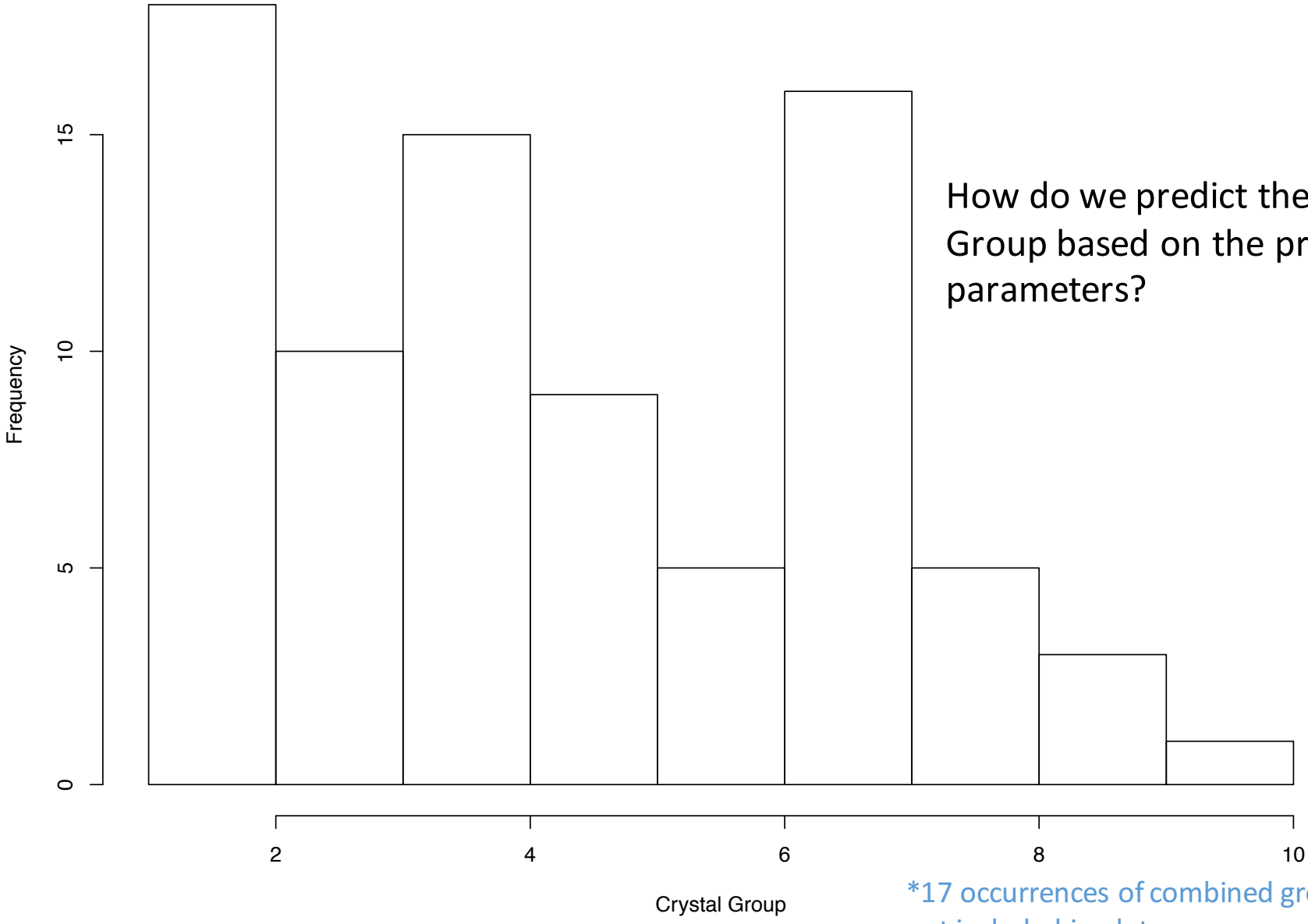
A more realistic model…

Crystal Group



*17 occurrences of combined groups– not included in plot

Crystal Group

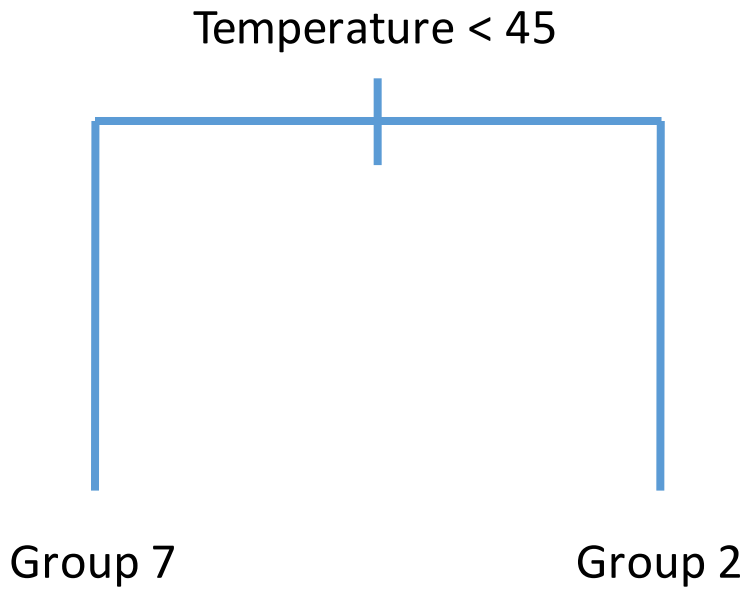


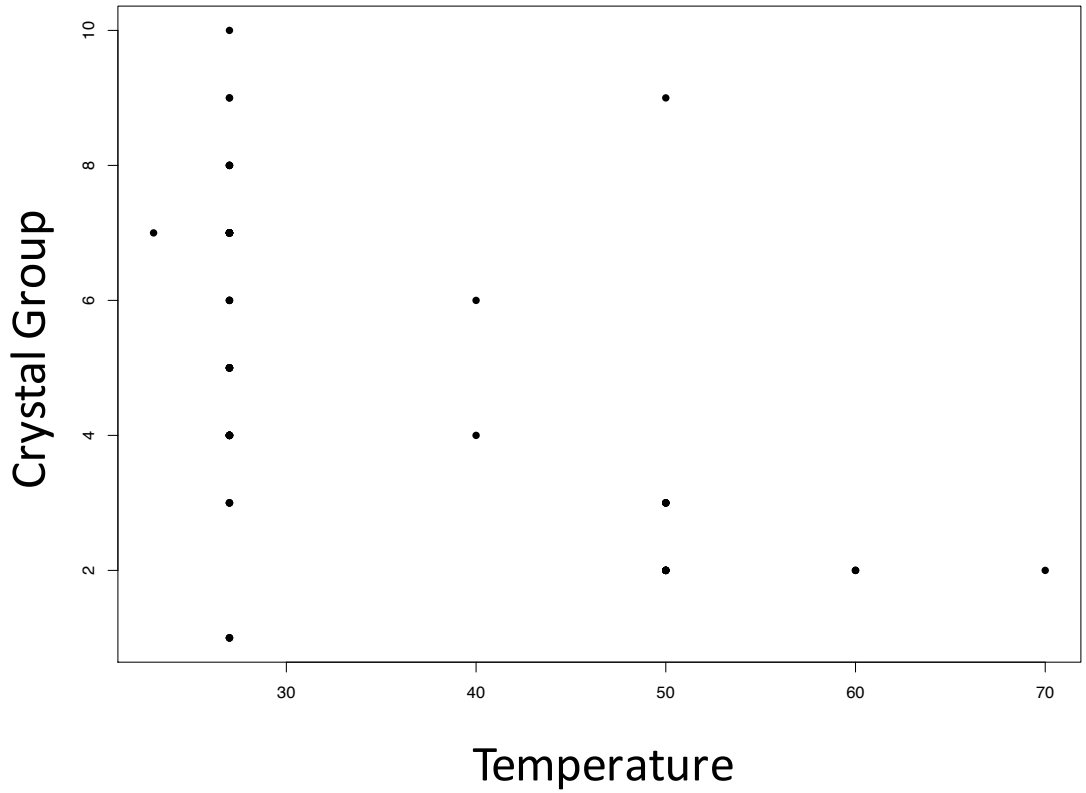
How do we predict the Crystal Group based on the production parameters?

*17 occurrences of combined groups– not included in plot

Temperature

- Temperature is the most distinguishing production parameter for Crystal Group.





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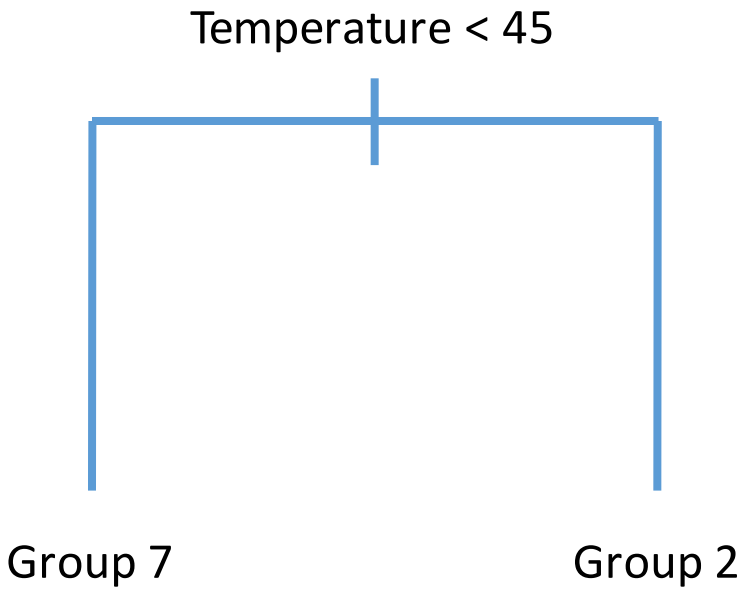
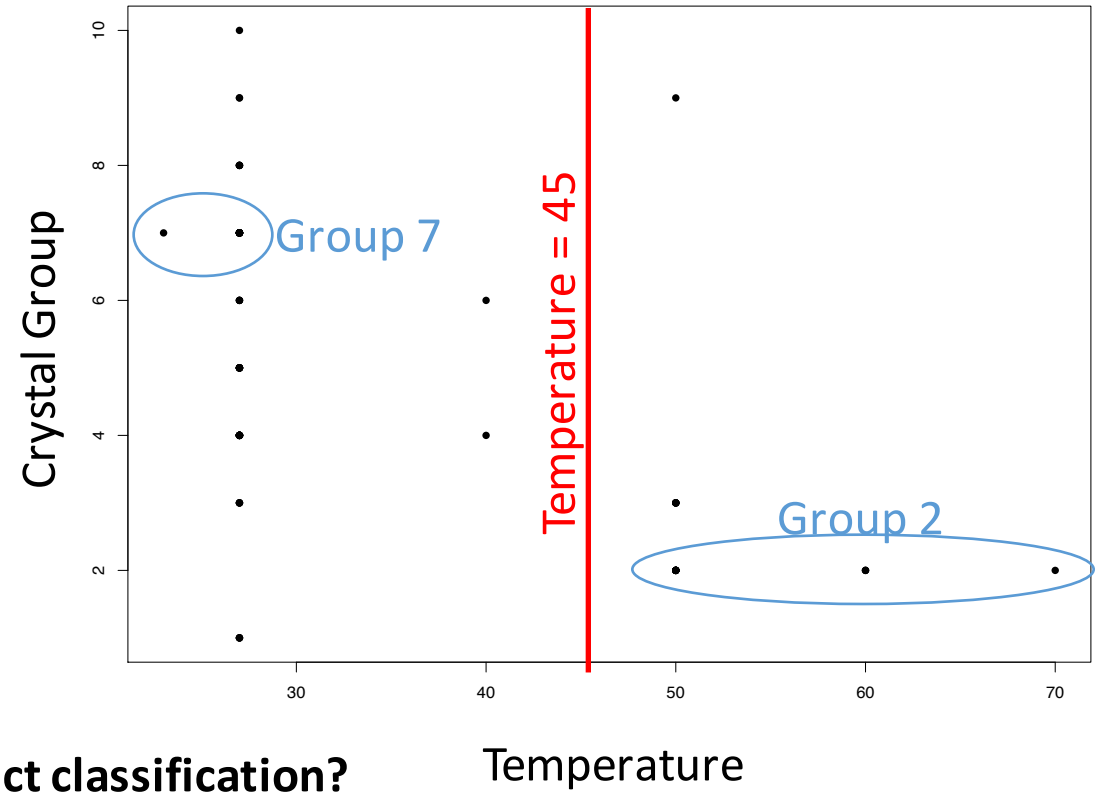




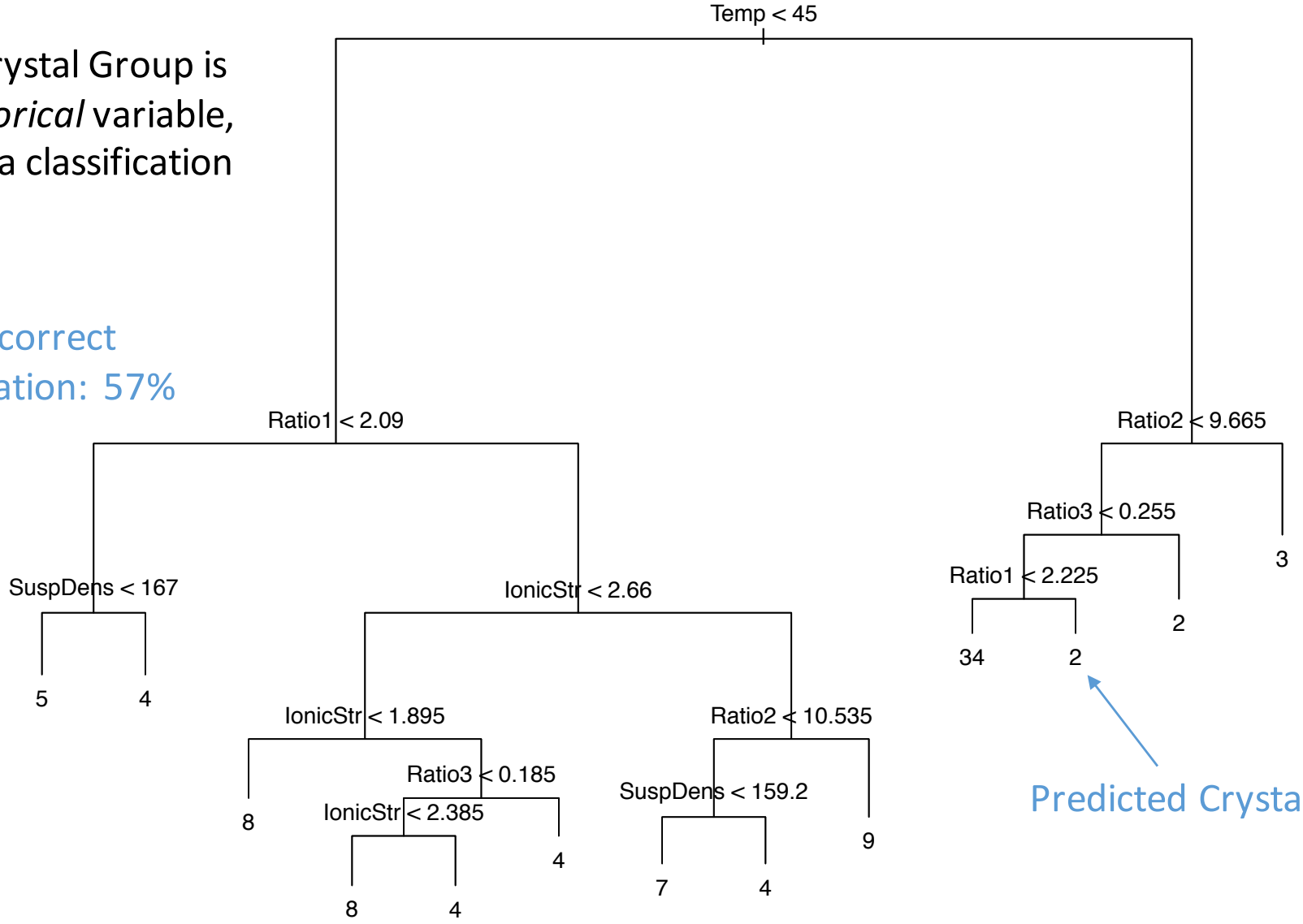
Correct classification: 33%

How do we increase the % correct classification?

Crystal Group Classification Tree

Since Crystal Group is a *categorical* variable, we use a classification tree…

Overall correct classification: 57%



Predicted Crystal Group

Run 114 for example…

Run	114
ResTime	13.4
SuspDens	147.9
AgitSpeed	1250
Ratio1	2.33
Ratio2	6.47
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IonicStr	1.93
Temp	27
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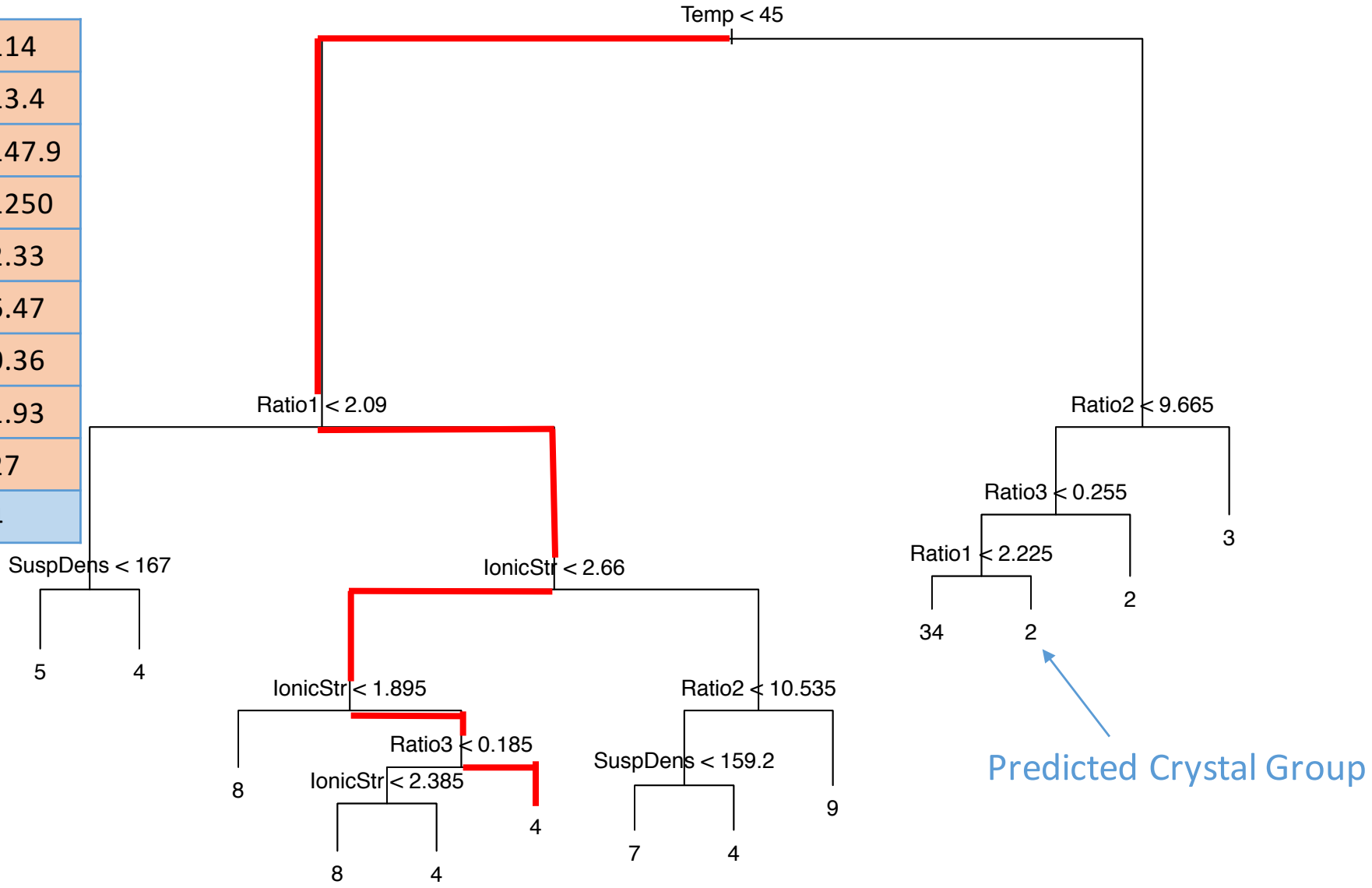

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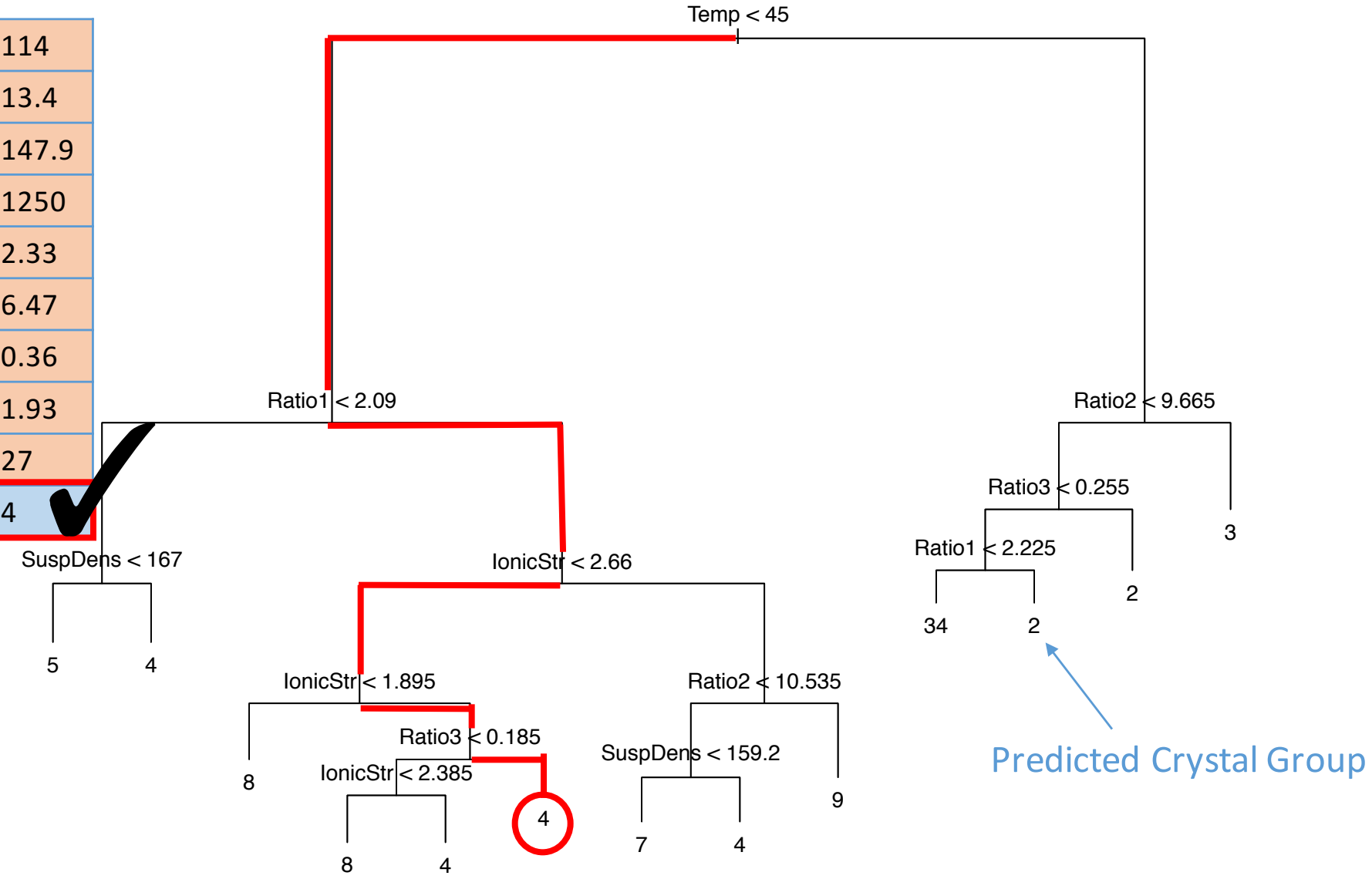

Discussion

- Different models are more appropriate for particular responses.
- Does measured PSD adequately represent the particle sizes present in the source material?
- Potential impacts from:
  - Continued agglomeration in slurry samples during counting delays
  - Adequate electrolyte saturation to avoid particle dissolution
  - Ability to replicate precipitation results

Thank you!

Questions?

References

- RC Hoyt. Characterization of Plutonium(IV) Oxalate Precipitation: An Overview of Experimental Work Performed During the 1980s at the U.S. Department of Energy Hanford Nuclear Reservation. PNNL-25530 (July 2016) Pacific Northwest National Laboratories, Richland, Washington 99352. Prepared for the U.S. Department of Energy under Contract DE-AC05-76RL01830.

Model Performance

Model & quality of fit R^2(R^2_{adj})

Response	1st order	1st order w/log	1st + int	1st + int w/log	ModelSel (use best of prev. models)	$DF_{ModelSel}$
NuclPopDensity	38% (33%)	38% (33%)	61% (38%)	85% (76%)	58% (49%)	17
GrowthRate	69% (66%)	69% (66%)	83% (73%)	84% (74%)	81% (77%)	20
NucRate	54% (50%)	54% (50%)	72% (55%)	71% (54%)	69% (62%)	17
AveSize	62% (59%)	62% (59%)	80% (68%)	80% (68%)	79% (73%)	21
Tot#Agg	47% (43%)	47% (43%)	67% (48%)	84% (75%)	64% (55%)	20
SolPu	50% (45%)	50% (45%)	91% (86%)	72% (55%)	91% (88%)	22
CalcEquil	47% (41%)	47% (41%)	98% (96%)	81% (68%)	98% (96%)	29
SurfArea	24% (17%)	24%(17%)	50% (18%)	47% (14%)	45% (30%)	20

Comments:

- Yellow highlight is model with the best **R^2** for a particular response.
- Removed run as a factor
- Removed DomSize response- similar to AveSize

Model Performance

Model & quality of fit R^2(R^2_{adj})

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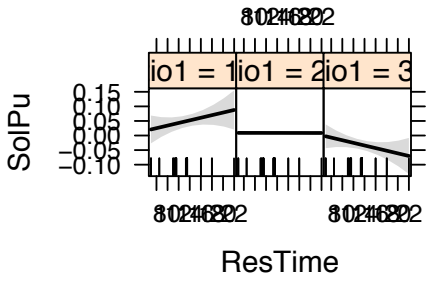
SolPu	50% (45%)	50% (45%)	91% (86%)	72% (55%)	91% (88%)	22
CalcEquil	47% (41%)	47% (41%)	98% (96%)	81% (68%)	98% (96%)	29
SurfArea	24% (17%)	24%(17%)	50% (18%)	47% (14%)	45% (30%)	20

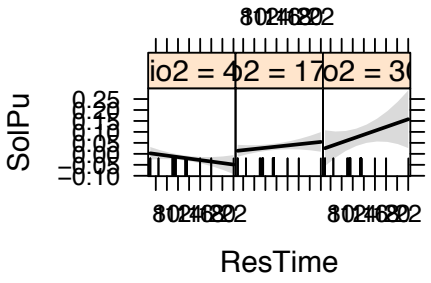
Comments:

- Being able to model CalcEquil well is a good implementation check- direct relationship with the inputs.

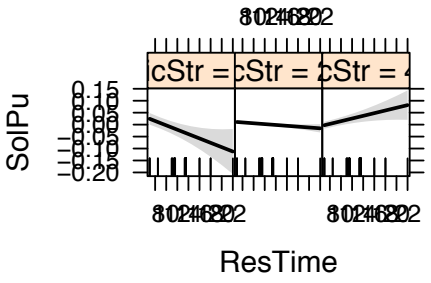
ResTime*Ratio1 effect plot



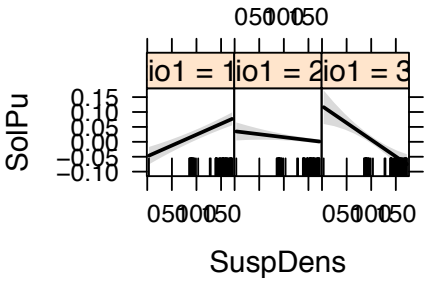
ResTime*Ratio2 effect plot



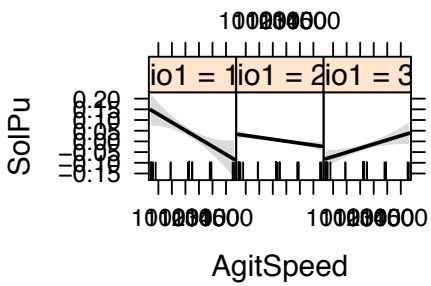
ResTime*IonicStr effect plot



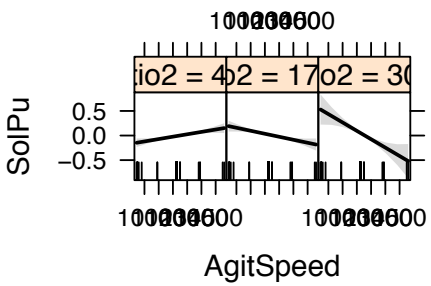
SuspDens*Ratio1 effect plot



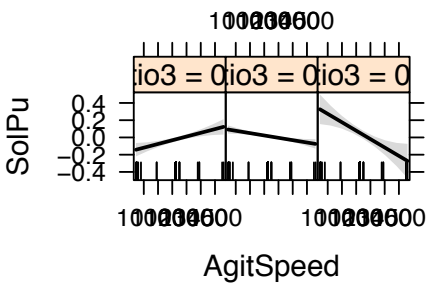
AgitSpeed*Ratio1 effect plot



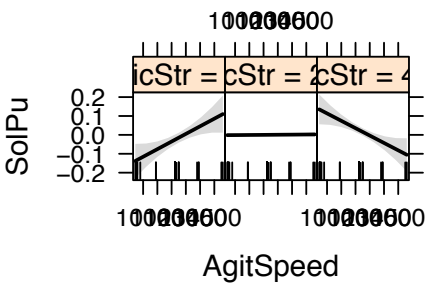
AgitSpeed*Ratio2 effect plot



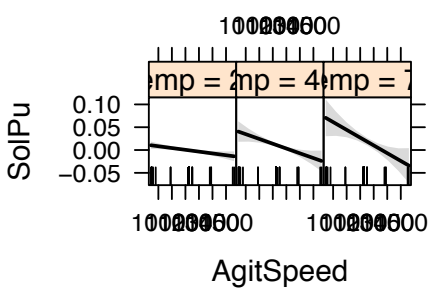
AgitSpeed*Ratio3 effect plot



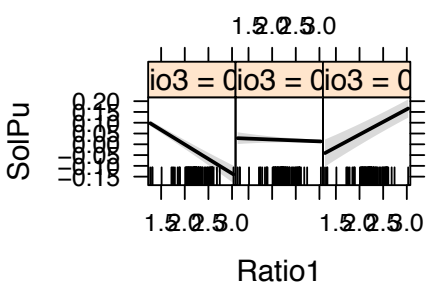
AgitSpeed*IonicStr effect plot



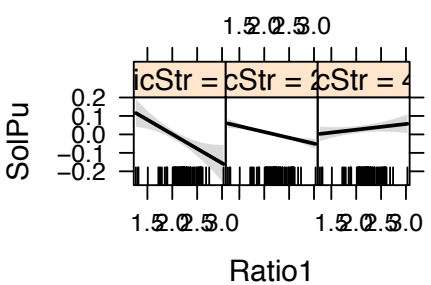
AgitSpeed*Temp effect plot



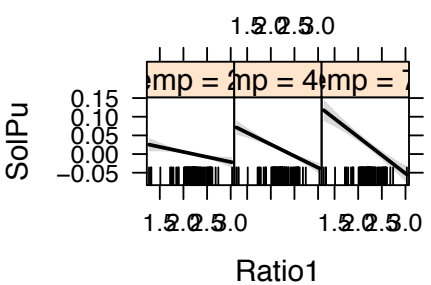
Ratio1*Ratio3 effect plot



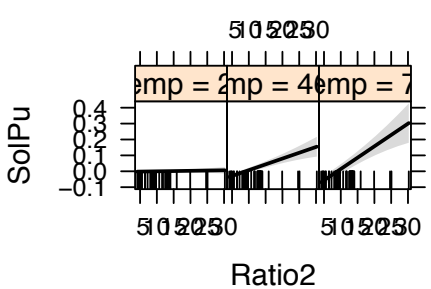
Ratio1*IonicStr effect plot



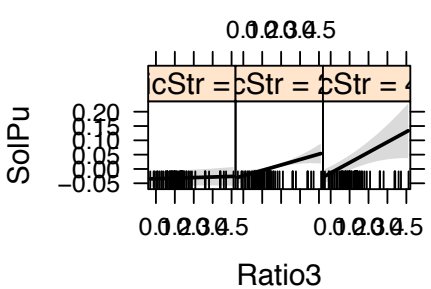
Ratio1*Temp effect plot



Ratio2*Temp effect plot



Ratio3*IonicStr effect plot



All Effects Plots for Soluble Pu

Data Nuances → and solutions

- Outliers
  → Removed 3 outliers
- Some runs have multiple Crystal Groups
  → Recoded the combination as their own group
- Delay after dilution for counting, SEM measurements were rescanned one year later
  → Averaged responses
- Particle size distribution measurements were taken 1.75, 2.75, 3.75, 23, and 47 hrs after the run was terminated.
  → Averaged responses
- Some runs had no response value
  → Coded as NA
- Saturated/unsaturated electrolytes were provided for a subsample
  → Averaged responses

…in order to keep one unique run per row.