Utilizing VisiMix to Assist Energetic Material Process Development

Jerry Salan
jerry.salan@nalasengineering.com
860-861-3691

Matt Jorgensen
matt.jorgensen@nalasengineering.com

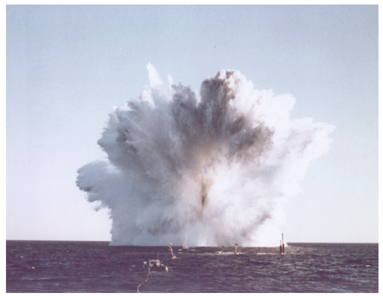
Available for public release

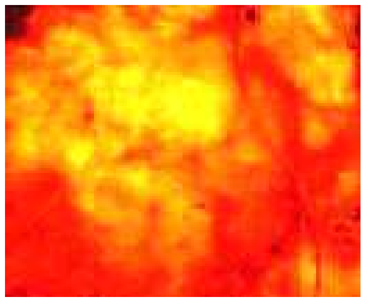
What do we do?

- Transition ***chemical processes*** to the plant environment
  - Identify engineering challenges including heat transfer, mass transfer, and mixing
  - Evaluate chemistry in the laboratory using *in situ* tools (IR, Raman, FBRM, PVM, heat flow)
- Evaluate pilot and production equipment. Validate processes through scale-down experiments
- Develop low-cost chemical *processes*
  - Fine Chemical
  - Pharma
  - Energetics

Energetic Materials
Simply *Special Chemicals*

- Explosives, propellants, pyrotechnics, reactive materials, related chemicals and fuels, and their application in propulsion systems and ordnance





USS Forrestal, CVA-59

- Zuni rocket misfired from an F-4 Phantom, impacting an armed A-4 Skyhawk fuel tank and resulting in fuel fire.
- Killed 134, injured 161, destroyed over 20 aircraft and cost the Navy $72 million

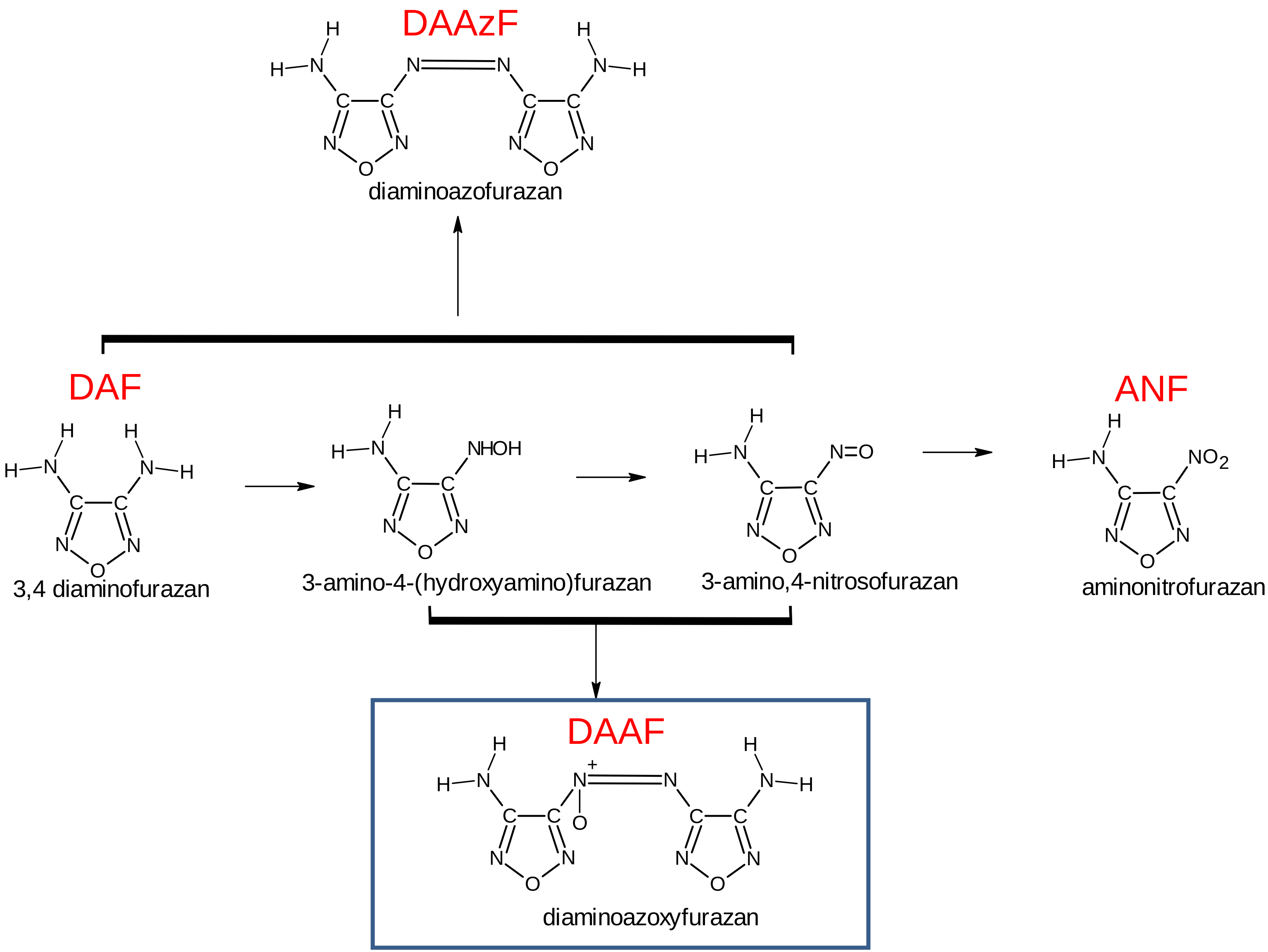
July, 1967

UNCLASSIFIED

Technical Outline

- Chemistry Background
- Processing Background
- pH challenges
- Morphology challenges
- Modeling using VisiMix
- Results
- Thank you

Insensitive Novel Energetics



Chemical Reactions

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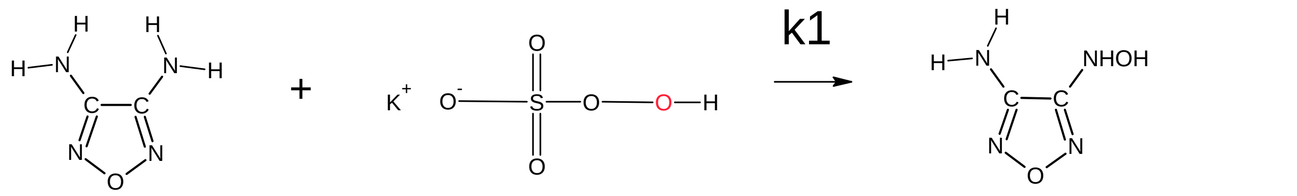
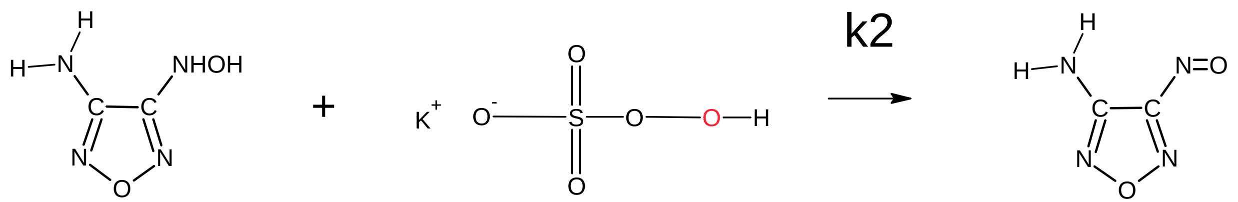
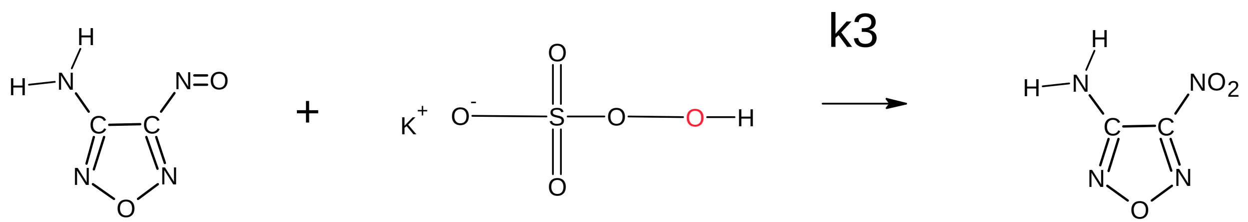
- Equation 1



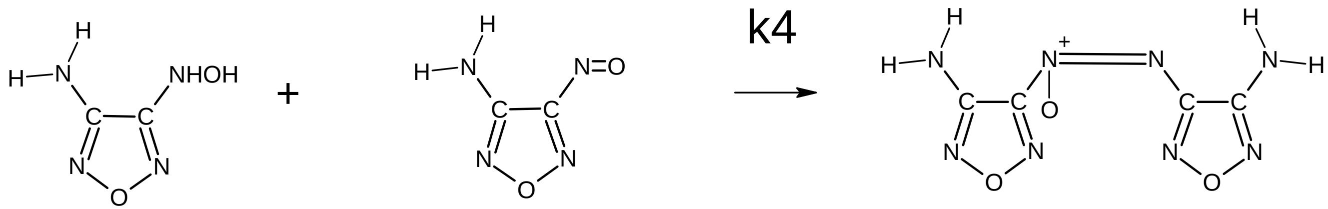
- Equation 2



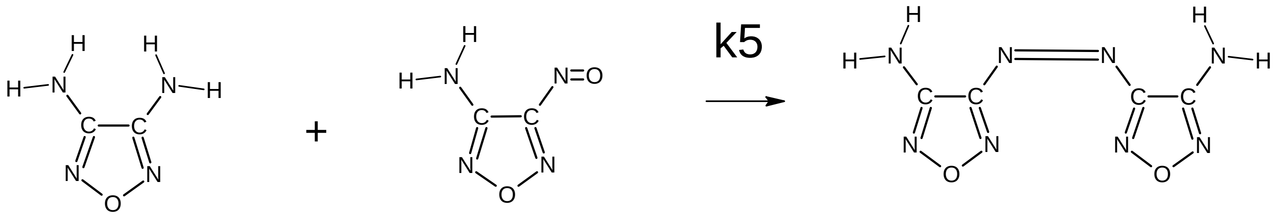
- Equation 3



- Equation 4



- Equation 5



Influence of pH

Lensovet Leningrad Technological Institute. Translated from Zhurnal Organicheskoi Khimii, Vol. 17, No. 4, pp. 861-865, April, 1981. Original article submitted June 12, 1980.

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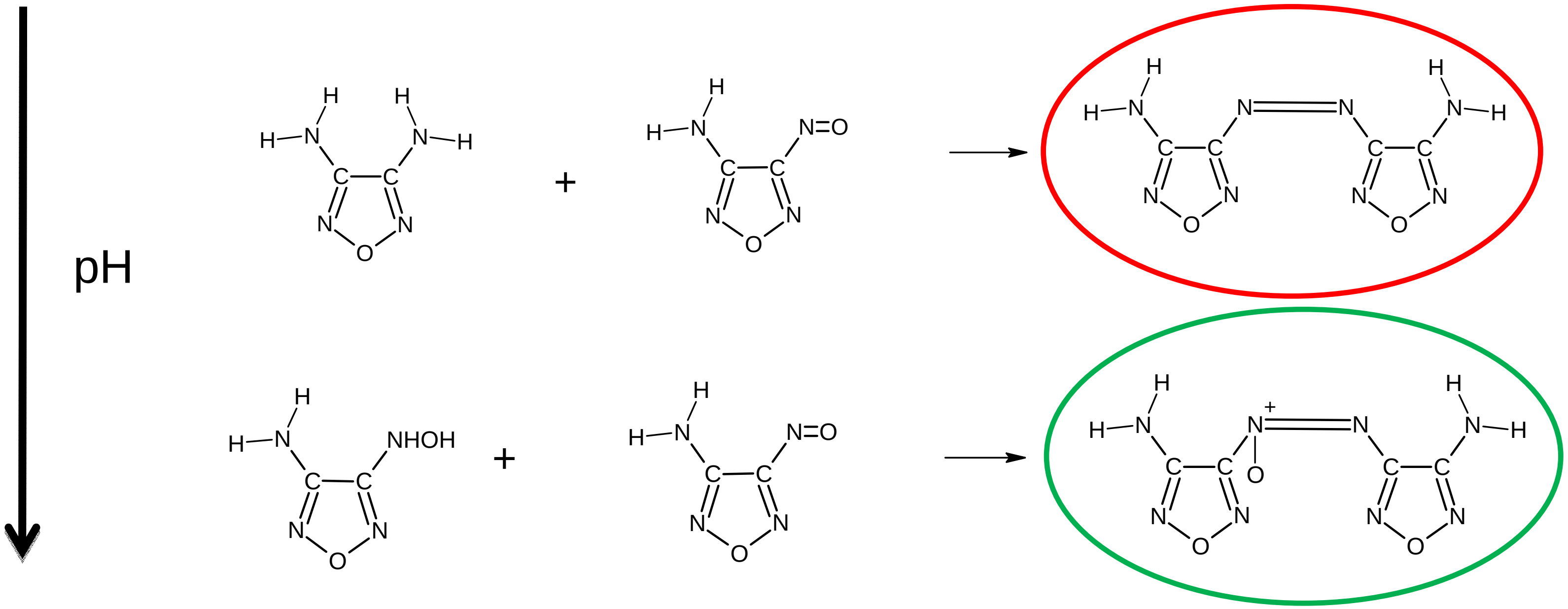


In contrast to the composition of the reaction products obtained during oxidation of the diaminofurazan (I) in an acidic medium, the oxidation of the diaminofurazan (I) in an aqueous medium leads to the formation of diaminoazofurazan (IV) (cf. expts. 8 and 9), and this is due to the significant increase in the concentration of the unprotonated diaminofurazan (I), which competes with 3-amino-4-(hydroxyamino)furzan in condensation with 3-amino-4-nitrosofurazan, in the reaction medium.

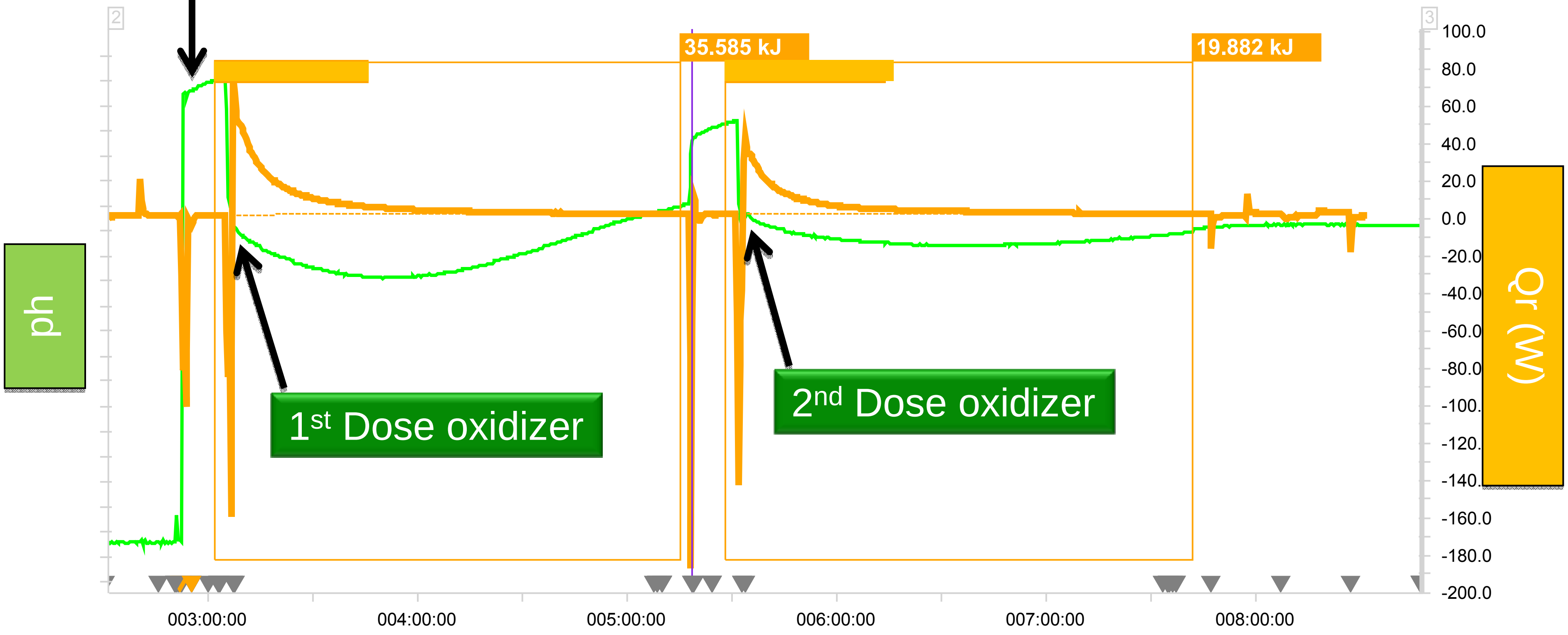
Why Continuous?
Batch Oxone Process

- Charge water to reactor
- Charge 3,4 diaminofurazan to reactor
- Charge sodium bicarbonate to reactor
- Charge oxidizer slowly to reactor (gas generation)
- 2nd charge sodium bicarbonate to reactor (pH adjustment)
- 2nd charge oxidizer to reactor
- Filter solids
- Challenges:
  - Low 'quantity per batch' yield (60 volumes of water)
  - Variable pH (challenging to optimize or reproduce on scale)
  - Mixing sensitive

Monitoring pH

In the pot = (1) water, (2) DAF, (3) sodium bicarbonate

1. Notice that ph varies as a function of time
2. Total heat includes heat of crystallization



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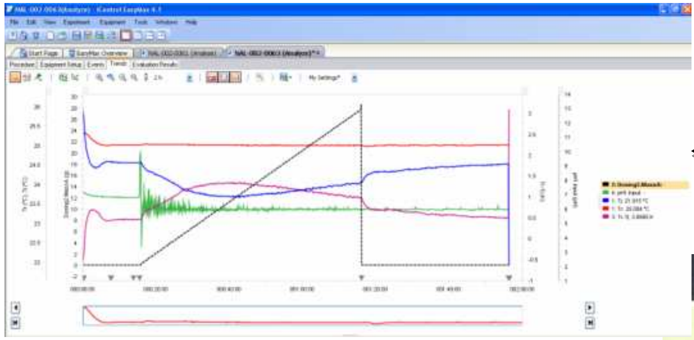
Engineering Challenges

- Foaming-this is a challenge during dose of Oxone™
- Influence of pH on purity and yield
  - Do we need to control pH?
- Large volumes of water
  - Waste generation
- Heat flow management
  - solubility
- Particle size control
  - Ideas include seeding to promote growth
  - Possibly continuous process

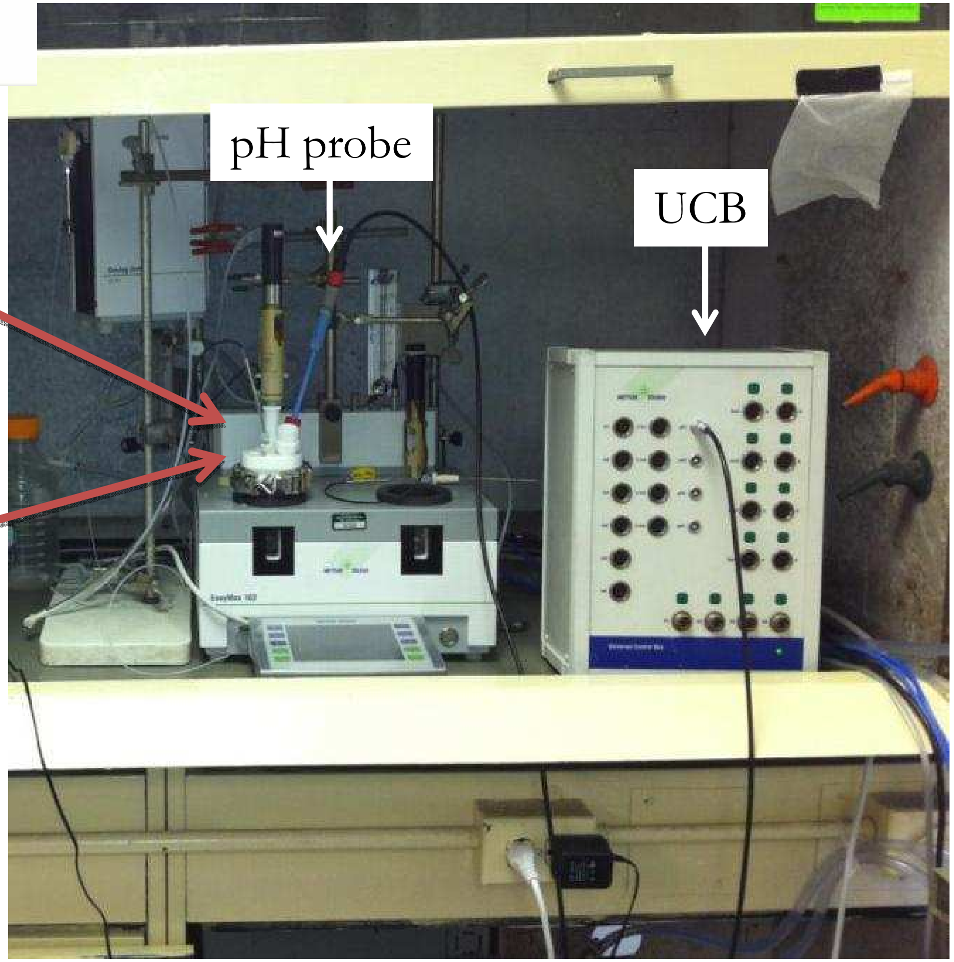
pH Feedback Control Loop



iControl-input desired pH

Oxone Feed

Sodium Carbonate Feed



Sodium Carbonate Pump output controlled by pH process variable

Why is pH so important?

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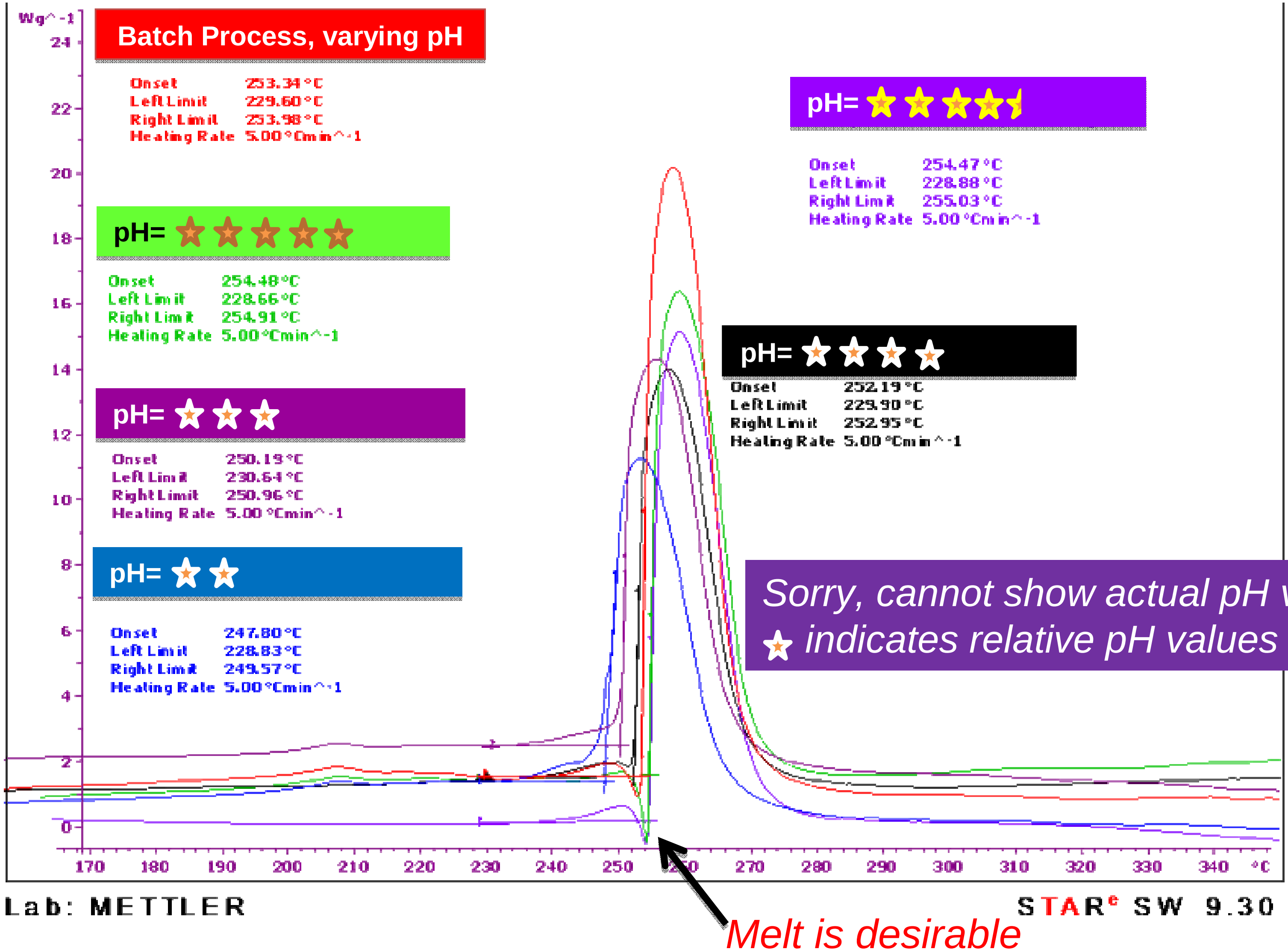

Sorry, cannot show actual pH values
★ indicates relative pH values

The lower pH results in increased level of an impurity. The impurity reduces thermal stability. Lower thermal stability increases violence of materials.

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EasyMax Screening Results

pH	Lot Number	Area Percent							
		DAF	ANF	DAAF	DAAzF	16.03 min	16.51 min	Isolated Yield	DSC Onset (℃)
Varies	BATCH	1.52	0.13	94.89	0.44	1.23	0.96	N/A	253.34
★★★	NAL-02-111	1.40	0.06	91.25	1.17	3.50	2.63	82.76%	250.19
★★★★	NAL-02-114	1.28	0.08	93.58	1.20	2.13	1.73	80.88%	252.19
★★★★½	NAL-02-134	1.25	0.08	95.51	0.42	1.37	0.99	75.41%	254.47
★★★★★	NAL-02-110	1.23	0.08	95.77	1.05	0.95	0.92	57.16%	254.48

↑ Thermal stability increases with increasing pH ↑

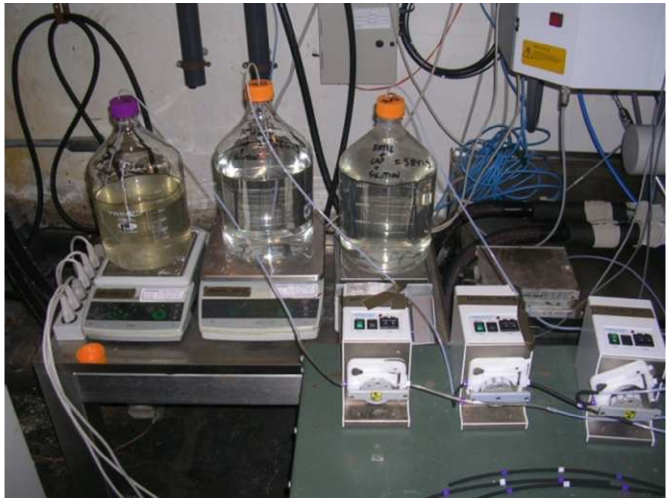
↓ Yield decreases with increasing pH ↑

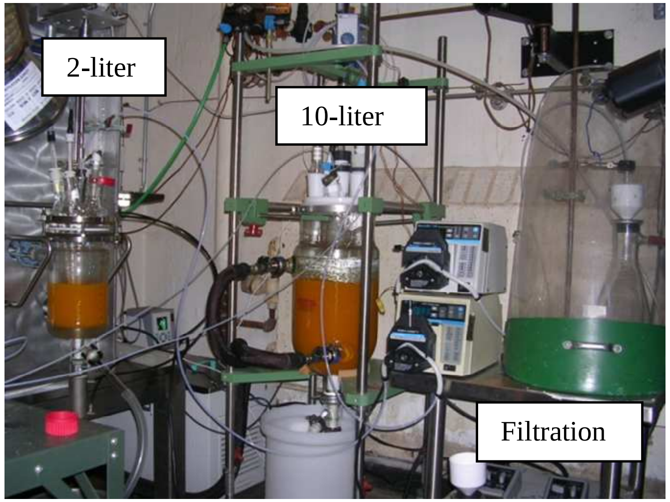
CSTRs in Series

Proof of Concept

- *Produced over 300-grams*
  - 2-liter and 10-liter in series
- Particle size distribution controlled with continuous process

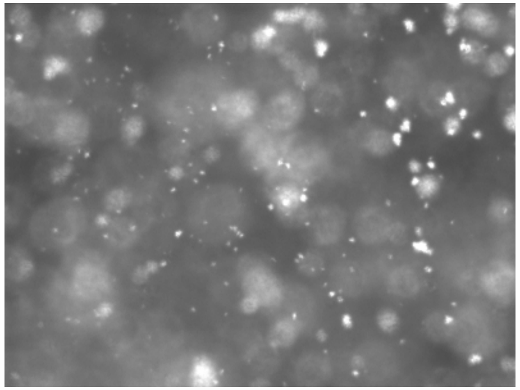
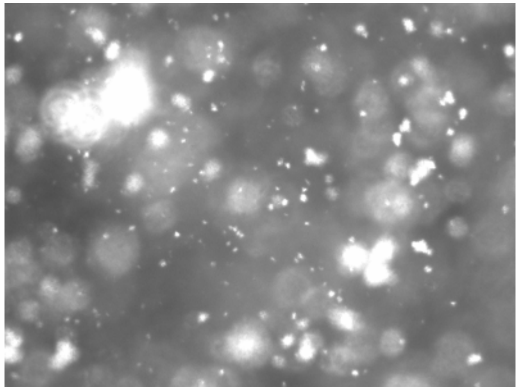
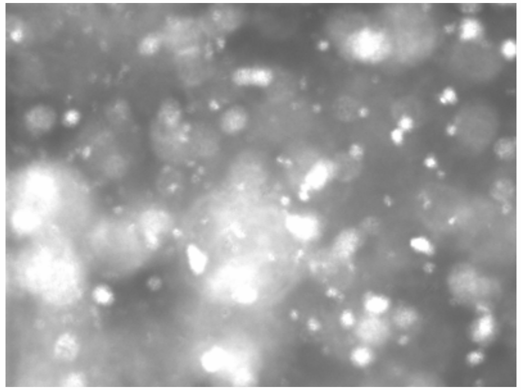
An RC1 can always double as a CSTR



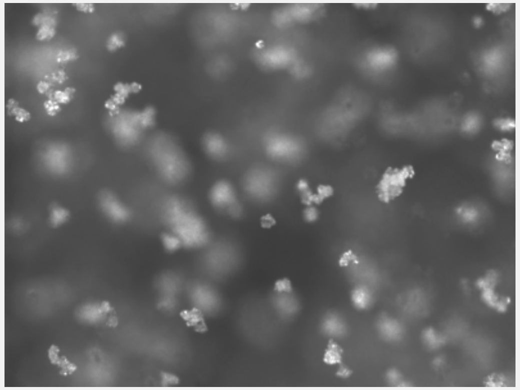
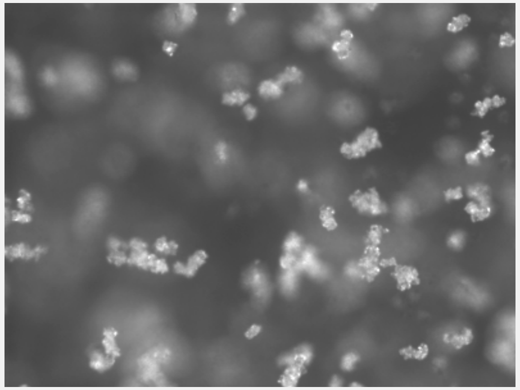
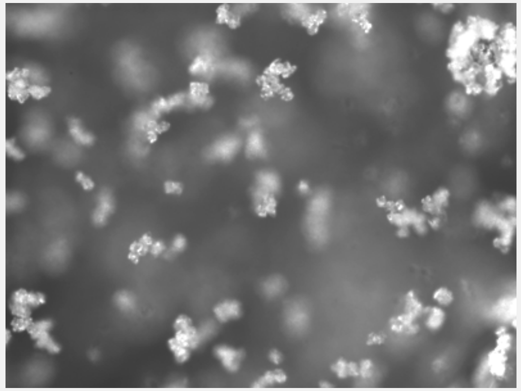


In-situ Camera-batch process

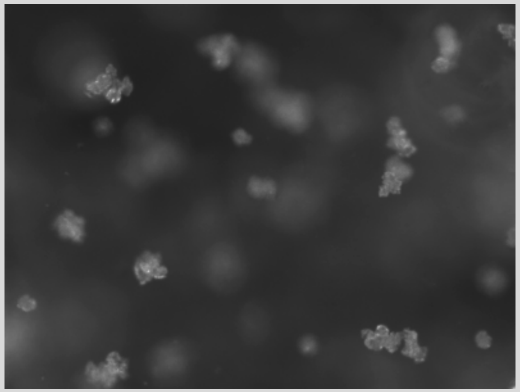
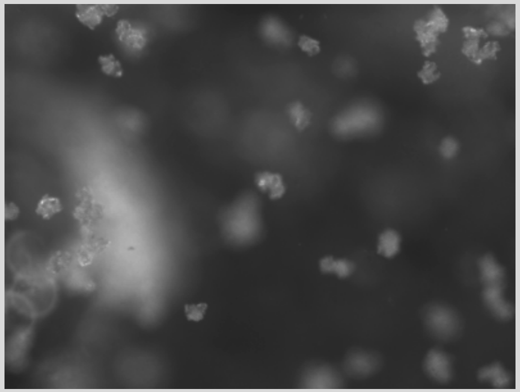
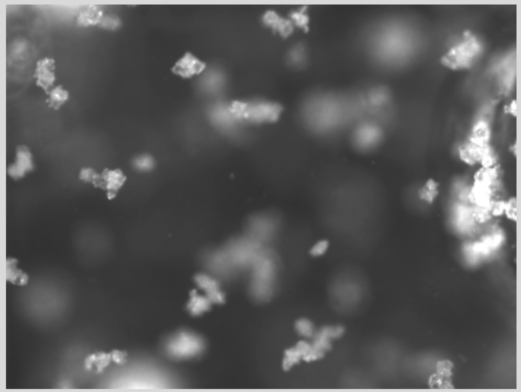
Just after 1st Dose of Oxone

After 1st Dose Oxone hold period

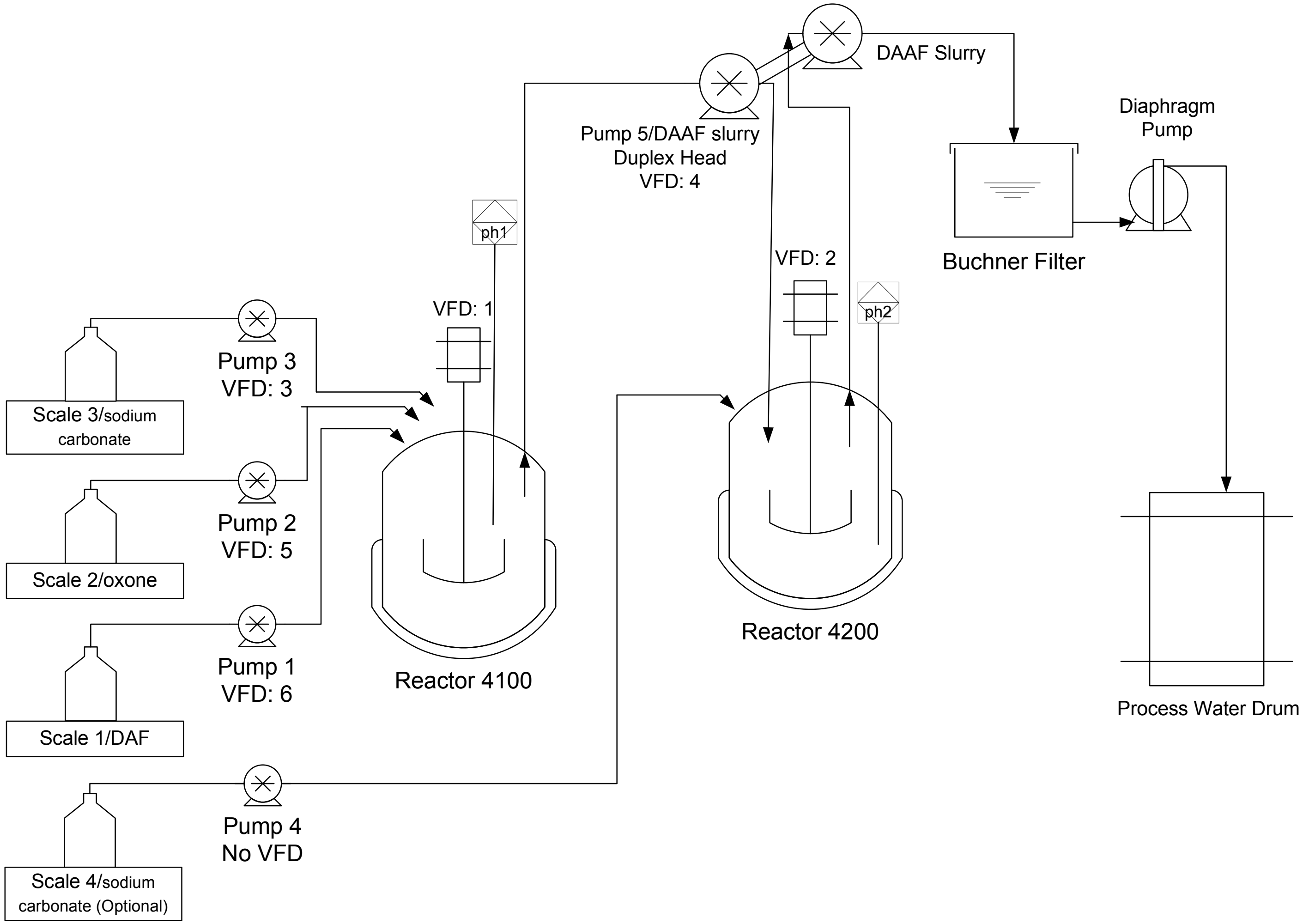




After 2nd Dose Oxone hold period

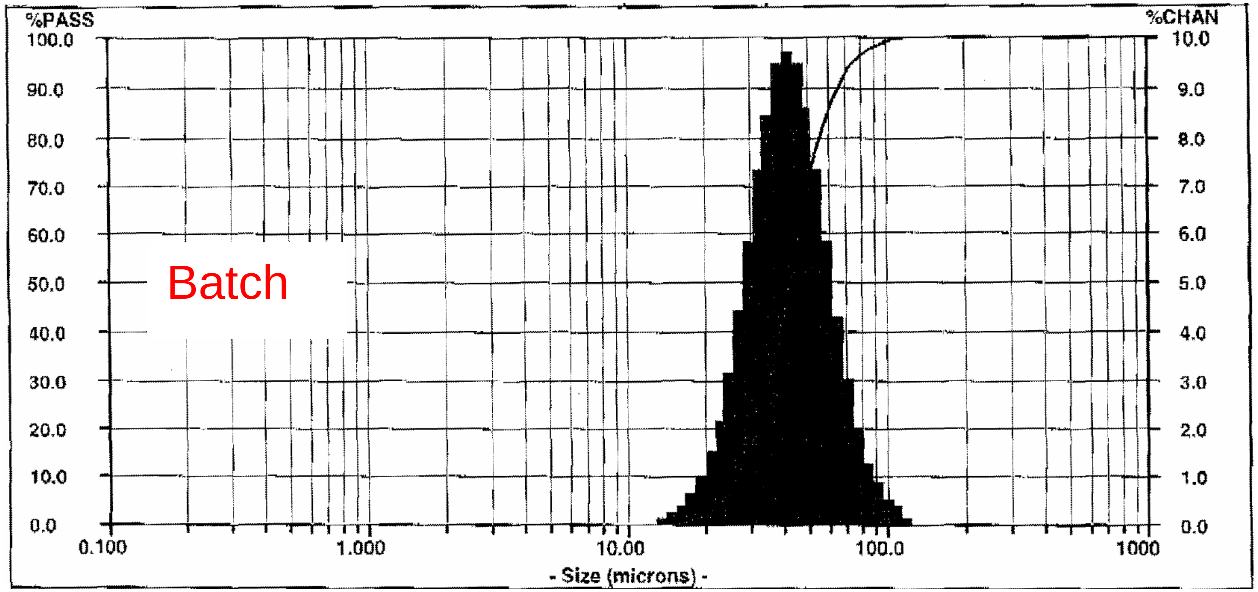




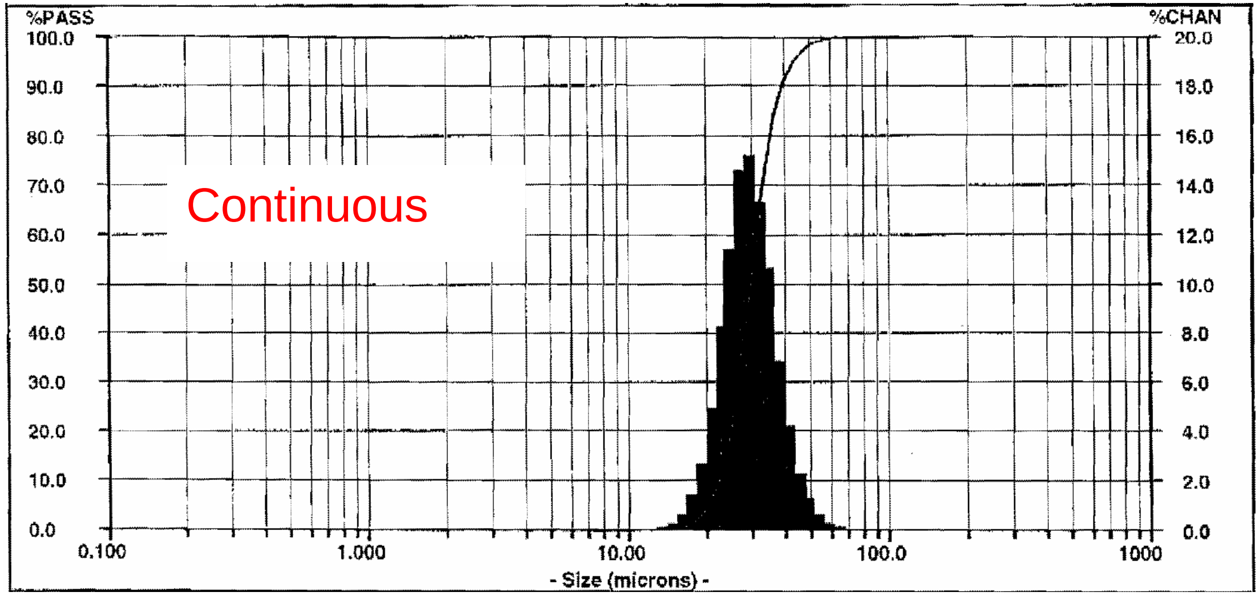

1
No. Measure Result
1 2 Points 99.13 um

Design of 50-liter CSTR

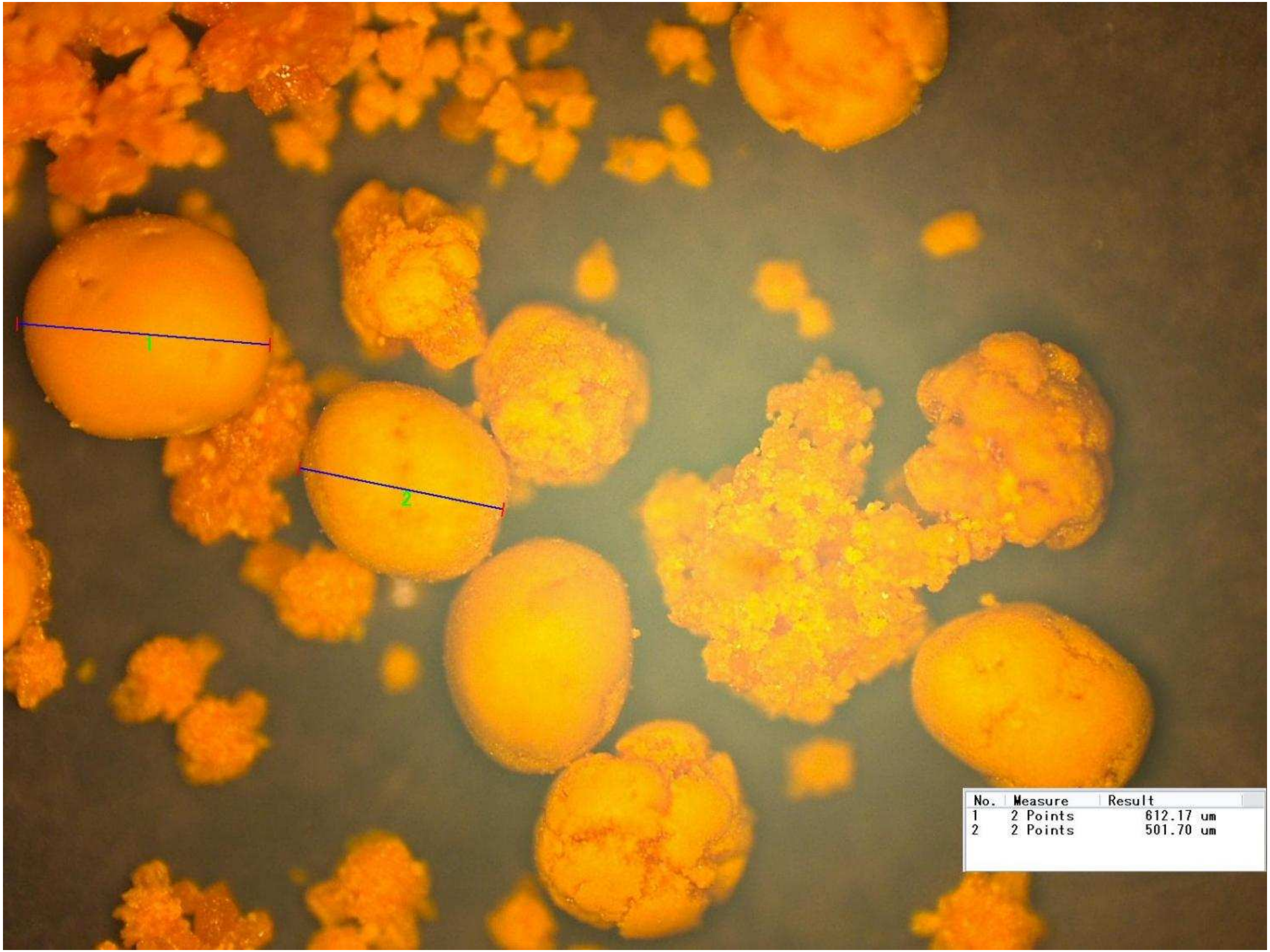


Particle Size Distribution





Two 50-liter CSTRs in Series


1
2
No. Measure Result
1 2 Points 612.17 um
2 2 Points 501.70 um

Reactor Design

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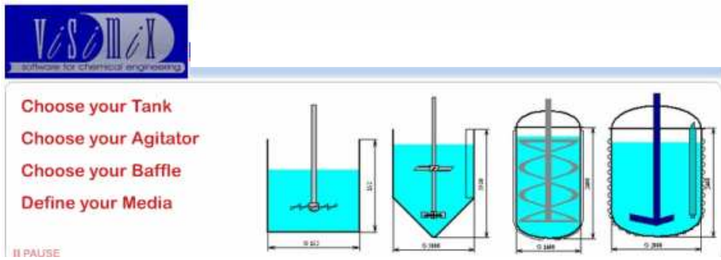
What does any of this have to do with VisiMix?

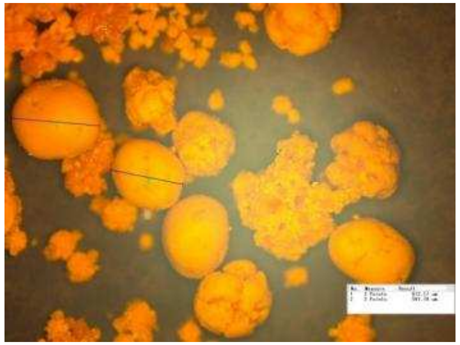
- Mixing Model
  - VisiMix
  - Validation
- Kinetic Model
  - Used DynoChem
  - Levenspiel plots
  - Validation
- Test support equipment
  - Pumps
  - pH control

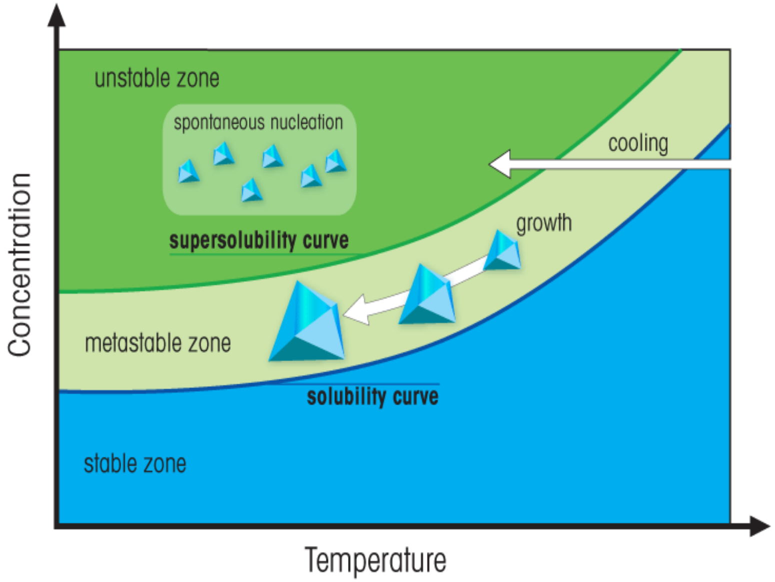


DynoChem®

Crystallization and Solids Dispersion

- Product is not soluble in water (solvent)
- Precipitation occurs immediately upon formation of product
- If crystals are present, growth and/or agglomeration may dominate over nucleation
- Poor dispersion may lead to some particles residence time being longer than others





Mixing Model

- Challenge 1: Monitoring and Control of pH
  - Poor mixing will result in pH electrode detecting an incorrect pH and continue to call for additional reagent after the correct amount has been added.
  - Poor mixing will result in gradients, resulting in impurities.
  - Location of pH probe could be critical
- Challenge 2: Solids dispersion
  - Poor mixing results in some solids being in the reactor train longer than other. This could influence particle size and agglomeration

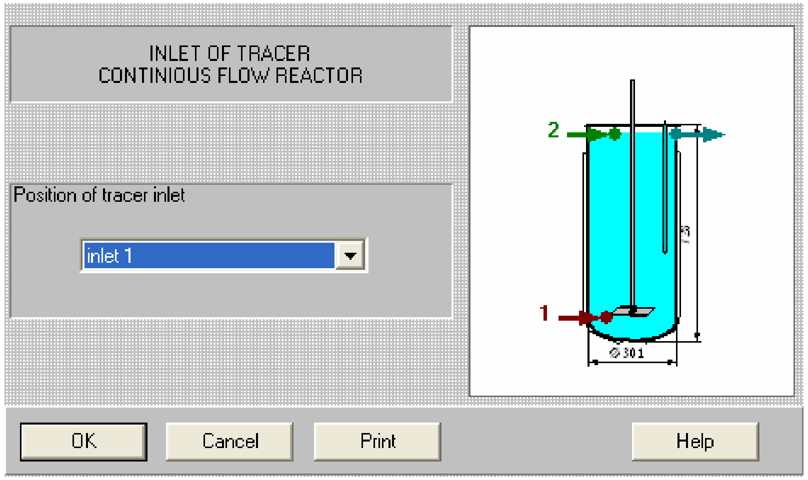
Scale-down Experiments

- Mixing parameters can be matched between EasyMax, RC1, lab-scale equipment, pilot-scale equipment and production equipment

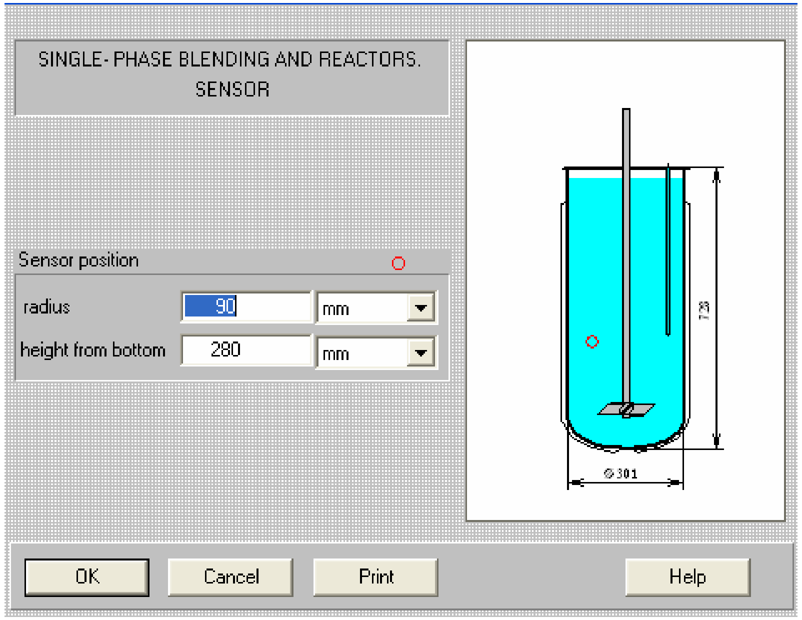
- Mixing challenges can be identified and resolved early in development

- It is pointless to generate data in the lab that is not representative of data that will be generated in the plant. A mixing sensitivity can make lab data useless and any resulting kinetic model generated from lab data.

Feed and Sensor Position for pH Control

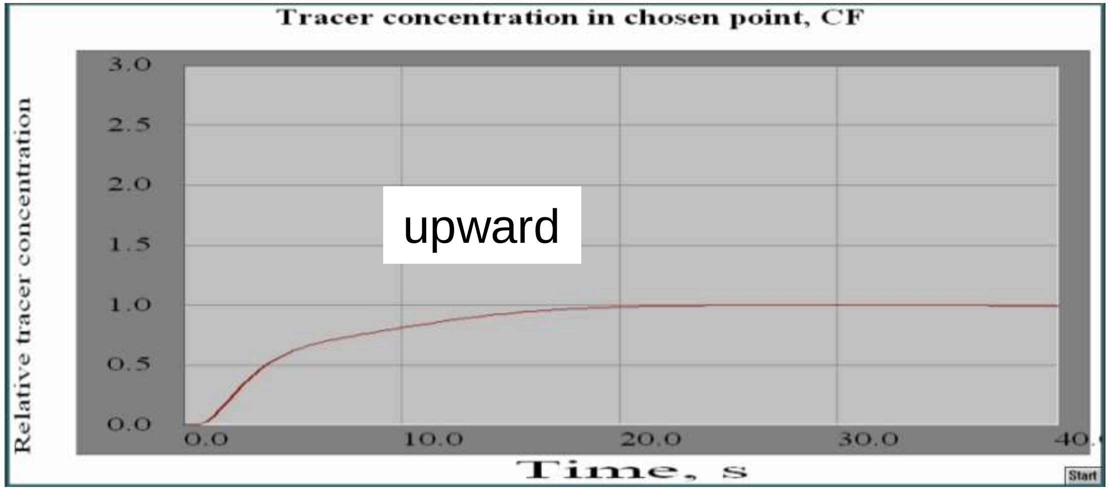


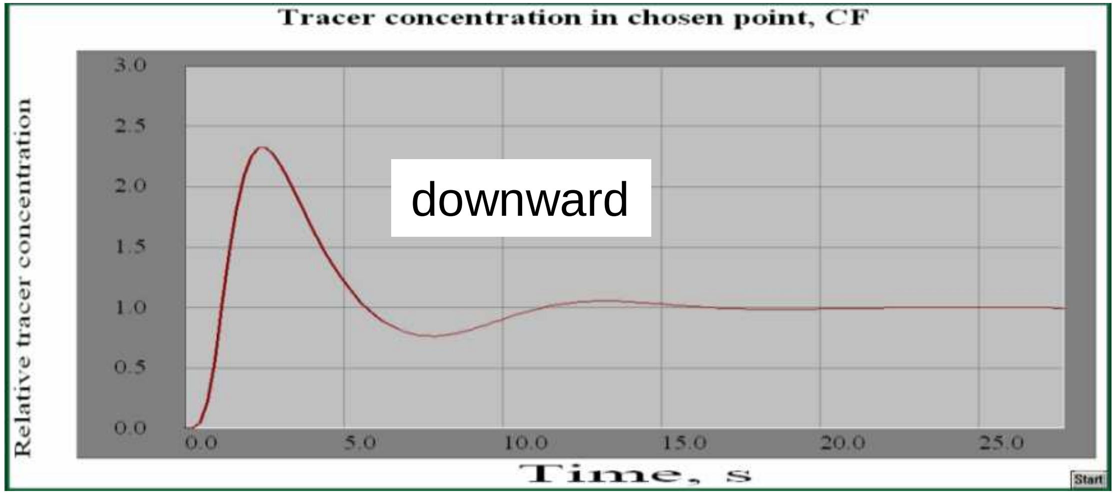
- Tracer exercise allows the user to evaluate location of feeds (1. Sodium carbonate feed and 2. Oxone feed)
- By imputing a tracer to the system and calculating the deviation over time, it is possible to compare reactor configurations to make decisions on optimum equipment choice.
- An example would be comparing up vs. down pumping impellers (next slide)

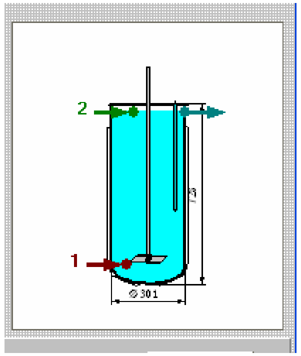


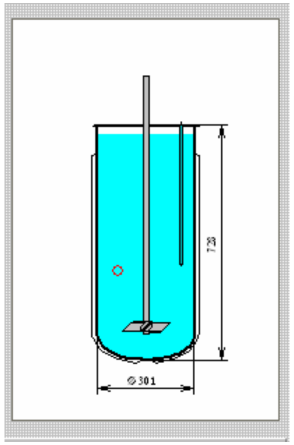
- VisiMix allows the user to evaluate the sensor location (will my sensor be in a location with good mixing?)

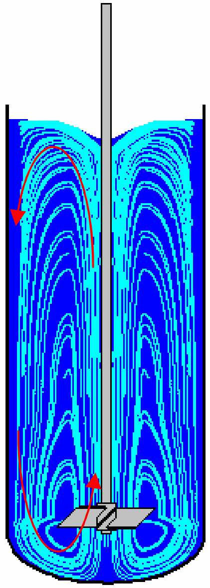
Up vs. Down Pumping Impeller Tracer Test

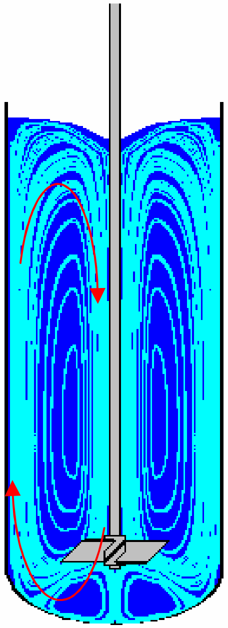






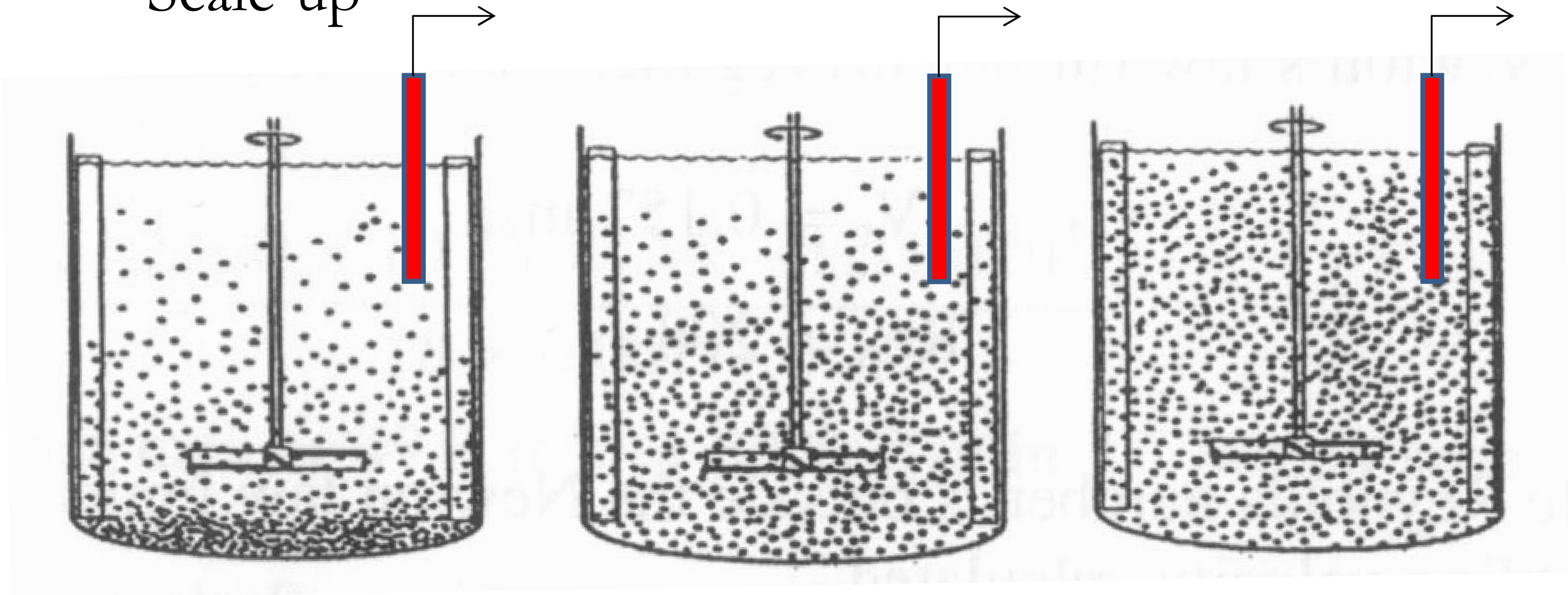






Solid-Liquid Mixing

- *Dispersion* of solids-physical process where solid particles or aggregates are suspended and dispersed by the action of the agitator in a fluid to achieve a uniform suspension or slurry.
- What about a *continuous* process?
  - Batch vs. continuous crystallization
  - Scale-up



Definitions

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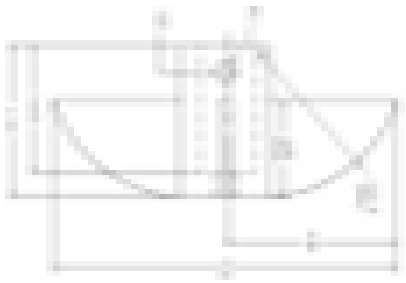
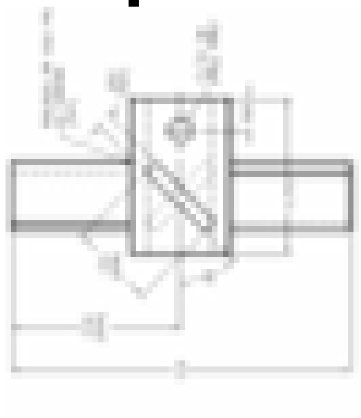
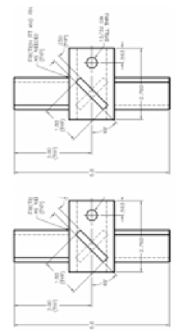
- Maximum degree of non-uniformity (axial, radial)
  - This parameter characterizes the maximum deviation in local concentrations of the solid phase from the average concentration in the tank. Complete uniformity of the solid phase distribution is not always necessary. However, if actual non-uniformity is higher than 25-30%, partial settling or flotation may occur.
- Average concentration of solid phase in continuous flow
  - This parameter is related to continuous flow processes. The concentration of the suspension in the outlet point is assumed to be equal to the concentration in the feed flow. The difference between the actual average concentration in the tank and the concentration in the flow depends on the degree of uniformity of axial and radial distributions and on the outlet position.
- Relative residence time of solid phase
  - This parameter is related to continuous flow processes, and is estimated as a relation of the mean residence time of the solid phase to the mean residence time of the suspension. Mean residence time of the solid phase depends on the relation of local concentration in the outlet point to the average concentration of the solid in the tank. The higher is the degree of uniformity of distribution, the smaller is the difference in the residence times for the solid and liquid phases. This difference can also be reduced by a correct choice of the outlet position.

Available Impellers



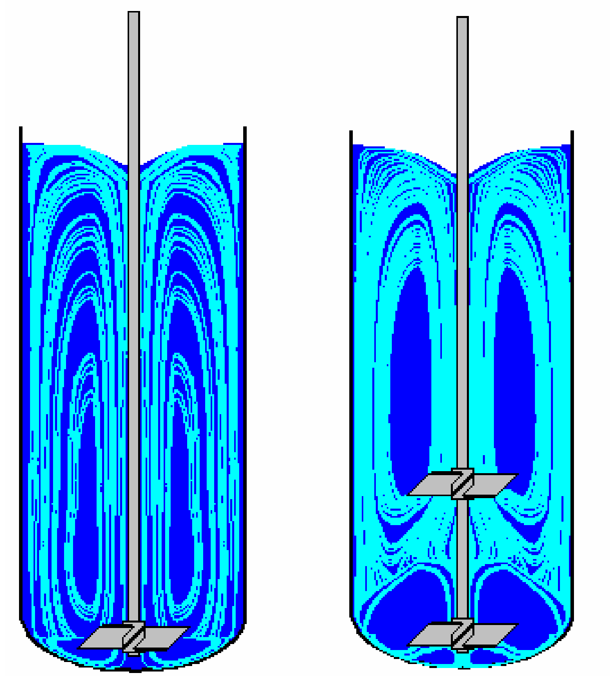


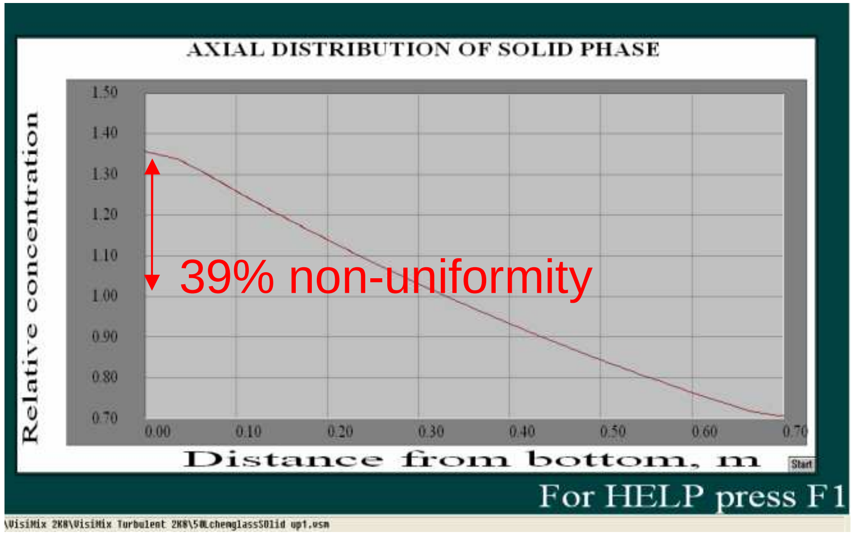


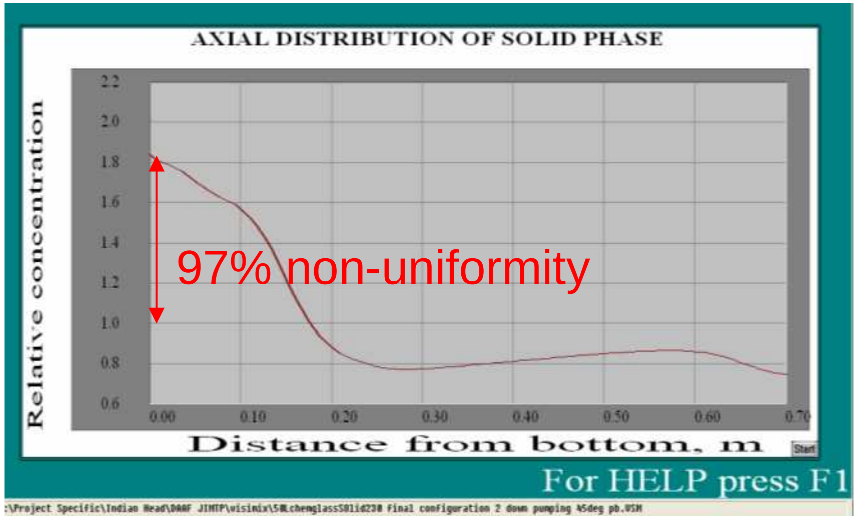
	Single paddle impeller 230 rpms	Single pitched impeller 230 rpms	Dual pitched impeller 230 rpms
Max degree of non-uniformity –axial, %	35.4	39.0	97.0
Average concentration of solid phase in continuous flow (kg/m^3)	6.32	6.08	6.86
Relative residence time (ratio)	1.27	1.32	1.17
Characteristic time of micro-mixing (sec)	4.63	3.79	2.79 ***Best for pH control***

Flow Patterns

- Dual impeller-second impeller actually interferes with flow pattern, resulting in higher degree of non-uniformity

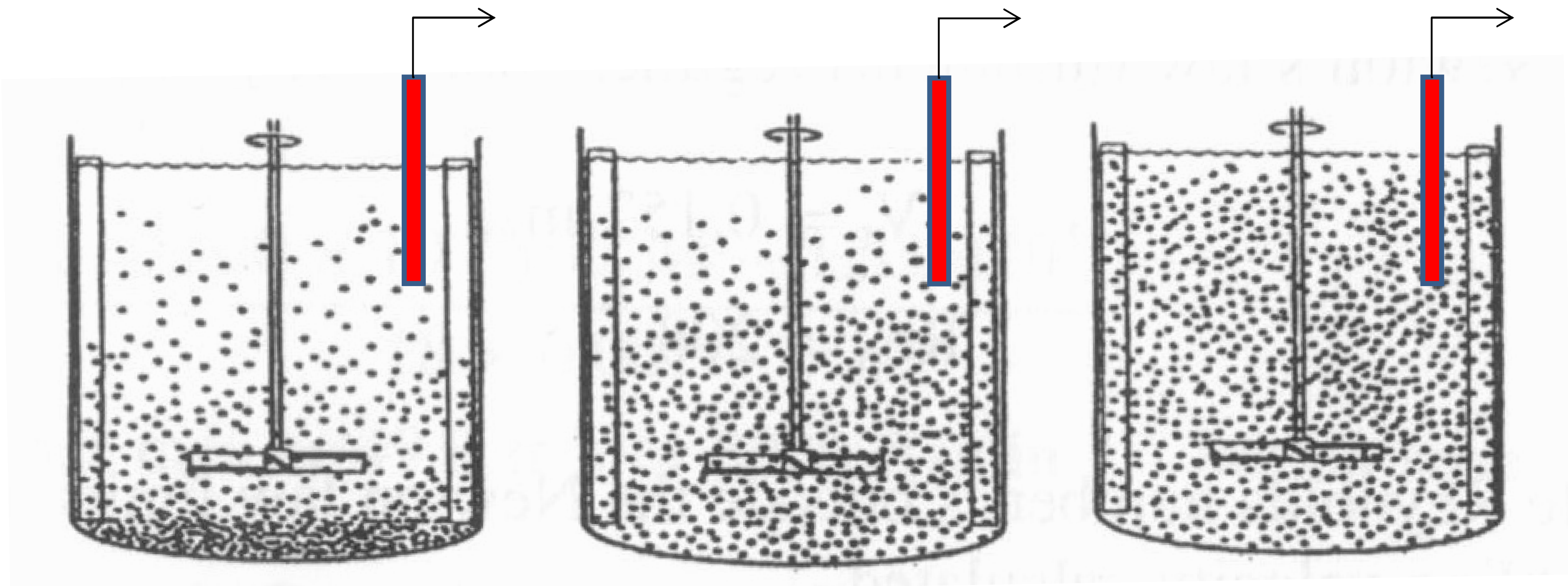




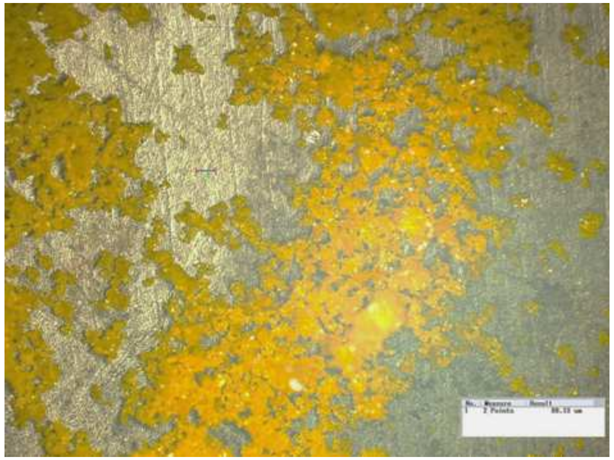


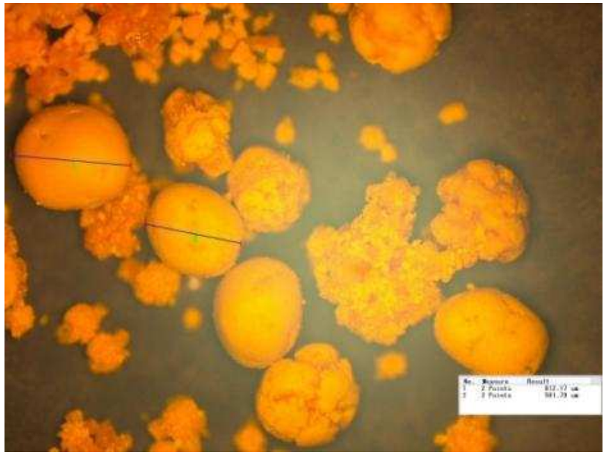
VisiMix Calculations

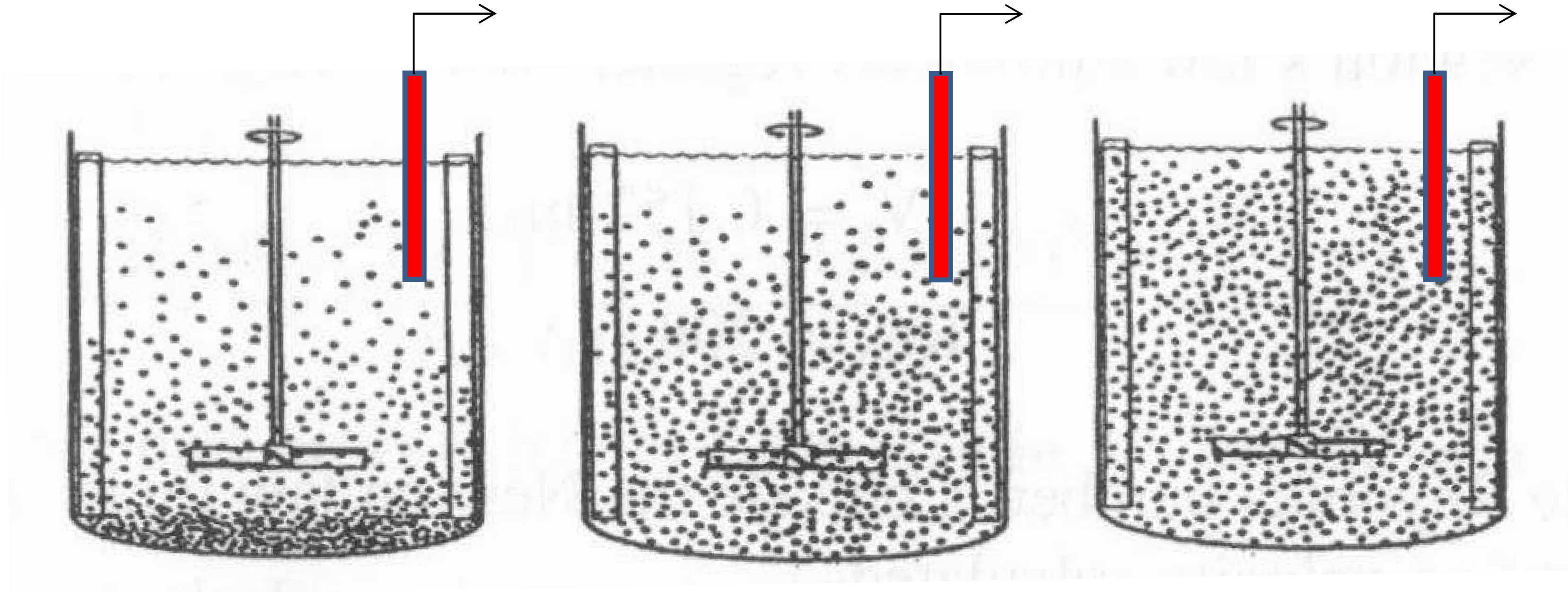
- Provide detailed analysis of equipment to which we scaled up
- Provide conditions for 'scale-down' experiments
- Allows for simple changes to be made in the model that are quite complex to do in the plant (i.e. change impeller, add baffle, change location of sensor, etc.)



Comparison







Summary

- Developed a continuous process to produce quantities of material safely
- Scale-up will always be a balance across various chemical engineering constraints
  - ***Mixing (our focus today)***
  - Heat flow
  - Kinetics
- VisiMix allows for quick and efficient investigations that minimize risk upon scale-up
- VisiMix allowed us to evaluate a specific reactor configuration, make appropriate changes and produce quantities of high quality material for our customer

Thank you

- Mr. Chuck Painter, Director, Navy ManTech Office
- Mr. Tod Ricks, NSWC Indian Head Division
- Mrs. Shilpa Amato, NSWC Indian Head Division
- Ms. Kim Hanson, NSWC Indian Head Division
- Ms. Elizabeth Francois, Los Alamos National Laboratory
- Dr. Dave Chavez, Los Alamos National Laboratory
- VisiMix
- Mettler Toledo AutoChem
- Mr. Matt Jorgensen and Ms. Shannon Lenahan, Nalas Engineering