Inherently Safer Design / Technology of Stirred Reactors. VisiMix® Approach

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Introduction:

This presentation is devoted to the VisiMix® application for improvement of the Inherently Safer characteristics of stirred reactors.

According to Dennis C. Hendershot (see his paper "*Inherently safer chemical process design*" in *J. Loss Prev. Process Ind*. Vol.10, No.3, pp.151-157. 1997) "*A chemical manufacturing process could be described as **inherently safer** if it reduces or eliminates one or more hazards associated with the materials and operations used in the process, when compared to some alternative process, and this reduction or elimination is accomplished by characteristics which are permanent and inseparable parts of the process*." And the process engineer has to "*identify ways to eliminate the hazards associated with the process, rather than to develop add-on barriers to protect people from these hazards" using "appropriate analytical and decision making tools to select him the best overall process alternative, considering all of the hazards*."

Introduction (cont’d):

Till now we (the VisiMix® team) were not deeply involved in this subject. A set of the VisiMix® software codes was developed for process engineers as a tool for simulation and technical calculation of stirred reactors and their operation conditions. But we believe that VisiMix® potential enables to extend its field of application and use it to improve *Inherently Safer* characteristics of the considered stirred reactor that renders the VisiMix® an efficient tool for safety experts too at (**i**) reactor/process design stage; (**ii**) operation stage; (**iii**) accident/incident investigation.

Now we are developing a new VisiMix® version. This version will include a separate submenu named arbitrary as ***Inherently Safer Design/Technology Test*** and it is important for us to get your opinion about it.

<u>Motivation</u>:

1. Stirred reactors (***SR***) belong to the key type of equipment used in all branches of the chemical process industry (***CPI***). The SR operations are followed by ~14% of all accidents in Chemical Process Industry (***CPI***) caused by different reasons with 71% of them related to batch/semi-batch reactors operations. [*Kamarizan Kidam and Markku Hurme, Analysis of equipment failures as contributors to chemical process accidents. Process Safety and Environmental Protection, 91 (2013), pp. 61-78*].

<u>Motivation</u>:

2. The Inherently Safer Design/Technology (***ISD / IST***) concept requires that “the designer must apply good judgment and appropriate analytical and decision making tools to allow him to select the best overall process alternative, considering all the hazards” [*D.C. Hendershot, Inherently Safer chemical process design. Journal of Loss Prevention in the Process Industries, Vol.10, (1997), pp. 151…157*].

Background – VisiMix® Main features

1. The VisiMix® set of software tools is intended for technical calculation and simulation of mixing related processes [www.visimix.com].
   The VisiMix® was developed for *process engineers* as a universal tool for solving a wide range of technological problems.
   It gained recognition because it provides an adequate and a complete description of process and equipment configuration based on reliable models verified in practice.

Background (cont'd)

2. Main Unit Operation Topics (List conforms to *the VisiMix Turbulent®* and *VisiMix Laminar®* software tools)

Process / Unit Operation	Problem and Key Mixing Parameters
1. Basic mixing information	Main mixing characteristics
	Flow dynamics
	Vortex formation
	Turbulence, shear rates and stresses
2. Blending (distribution of a solute)	Mixing time
	Simulation of batch blending
	Micromixing
3. Suspension (liquid-solid mixing)	Checking "non-settling" conditions
	Radial and axial distribution of solid phase
4. Dissolution of solid	Complete dissolution
	Simulation of a dissolution process
	Mass transfer characteristics

Background (cont'd)

2. Main Unit Operation Topics (cont'd)

Process / Unit operation	Problem and Key Mixing Parameters
5. Leaching (liquid-solid extraction)	Collisions of particles
	Mass transfer characteristics
	Radial and axial distribution of solid phase
	Local shear rates and shear stresses
6. Crystallization	Uniformity of mother solution
	Mixing parameters affecting nucleation and growth of crystals
	Scaling-up parameters
7. Emulsification (liquid-liquid mixing)	Characteristics of emulsion
	Mixing parameters affecting emulsification
8. Liquid extraction	Mass transfer characteristics
	Mixing parameters affecting liquid extraction
	Scaling-up parameters

Background (cont'd)

2. Main Unit Operation Topics (cont'd)

Process / Unit Operation	Problem and Key Mixing Parameters
9. Single phase chemical reaction (batch reactor)	Process simulation
	Local concentration of reactants
	Non-uniformity of mixing in reactor
	Selectivity of reaction
	Scaling-up parameters
10. Single phase chemical reaction (semi-batch reactor)	Process simulation
	Local concentration of reactants
	Non-uniformity of mixing in reactor
	Selectivity of reaction
	Scaling-up parameters
11. Single phase chemical reaction (continuous flow reactor)	Dynamic characteristics
	Approach to "perfect mixing"
	Scaling-up parameters
12. Heterogeneous reaction (Liquid-liquid)	Mass transfer characteristics
	Mixing parameters affecting the reaction
	Scaling-up parameters

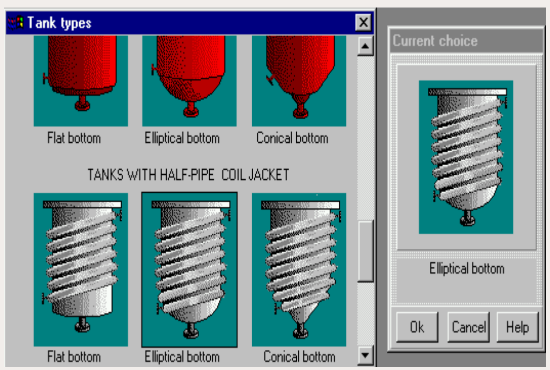
Background (cont'd)

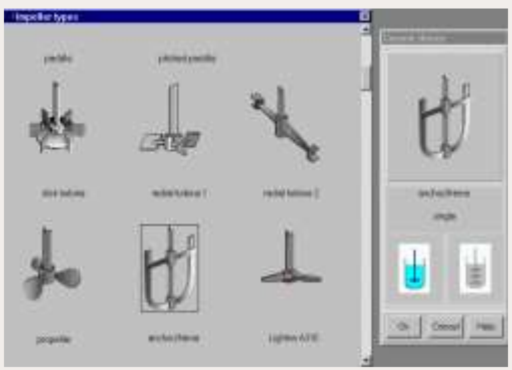
2. Main Unit Operation Topics (cont'd)

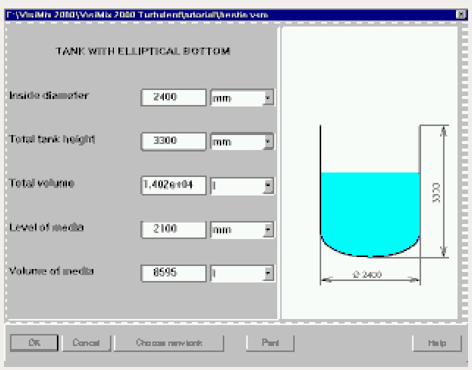
Process / Unit Operation	Problem and Key Mixing Parameters
13. Heterogeneous reaction. (Liquid-Solid)	Mass transfer characteristics
	Scaling-up parameters
14. Homogenization of multi-component mixture	Mixing parameters affecting the reaction
	Scaling-up parameters
15. Temperature-dependent reaction. Batch, Semi-batch and Continuous flow reactors	A comprehensive set of heat transfer characteristics
	Simulation of thermal regimes
16. Mechanical reliability	Stresses in dangerous cross-section
	Shaft vibration
17. Thermal safety	Analysis of runaway process
	Prediction of media overheating

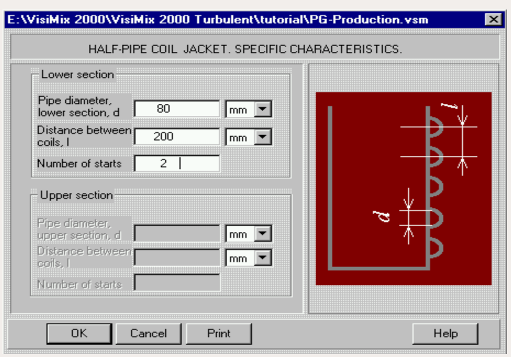
Background (cont’d)

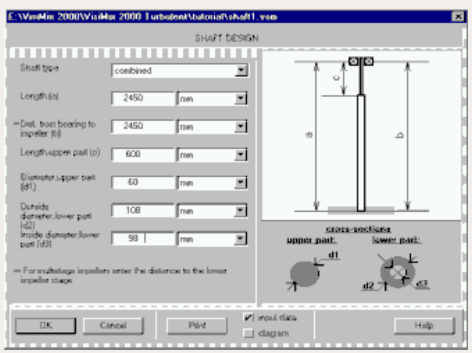
3a. All the Visimix® codes perform simulation of different technological processes with respect to *real equipment design* and *process regime parameters*. Selection of the equipment types and entering their parameters is effected by means of the *simple user-friendly graphic user interface* .











Background (cont'd)

3b. Besides for a user convenience, the simulation capabilities of the Visimix® software are sustained by means of build-in (**i**) *databases with properties of applied materials* and (**ii**) *HELP system with enhanced technical information* that endows it with properties of the reference source.

4. The Visimix® has a property of an *expert system* that analyses initial data and calculation results and issues *warning messages* whenever the input results in unacceptable process course. Hence, messages offer a mean to define safety range of the basic process parameters. Typical messages of the *VisiMix Turbulent*®, and *VisiMix Laminar*® codes are depicted in the next slide.

Background (cont’d)

Message	Possible reason	Hazard potential
Mixing power is too high for your drive	High viscosity or density of media. Incorrect drive selection	Possible unexpected stop of mixing. Shaft breaking (check Shaft design with Visimix).
Complete suspension is questionable	Big particle size for given mixing system. Too high concentration of solid phase.	Increase of bending moment and shaft/sealing breaking. Plugging of outlet from reactor. Hot spot formation.
Centrifugal separation of emulsion is expected. Addition baffles is advisable	Incorrect design for liquid- liquid mixing reactor	Decrease in dispergation ability of impeller and interface area Unpredicted reaction and mass transfer rate

Background (cont'd)

Message	Possible reason	Hazard potential
Vortex reaches impeller! Gas insertion from surface and shaft vibration are possible	Too intensive mixing. Not enough baffles resistance. Impeller too close to surface.	Shaft mechanical breaking. Unpredicted way of reaction. Foam formation. Unwanted oxidation.
After *XXX* sec have elapsed, the temperature falls outside the indicated range of process temperature	Weak heat transfer system. Too low mixing. Not proper design.	Unexpected way of the process. Agglomeration of solid particles, fouling of wall and damage to the heat transfer. Increase of pressure. Explosion.
This heat transfer agent doesn't correspond to process temperature range	Not proper heat transfer agent selection	Fail of heat transfer

Background (cont'd)

Message	Possible reason	Hazard potential
Rotational frequency of the shaft is too close to critical frequency. Vibrations are possible, see SHAFT VIBRATION CHARACTERISTICS	Small shaft diameter Unexpectedly high power	Shaft mechanical breaking
Fluid velocity is too low for efficient mixing	Not proper design	Unpredicted way of the process Damage to the product Plugging of the reactor
Inefficient mixing because of short-circuiting of flow in impeller area. See output parameters "Scheme of main circulation cycles" and "Circulation flow rate", and HELP		
Formation of stagnant zones is expected. For recommendations see HELP, Formation of stagnant zones		

Background (cont'd)

Thus if we recall that any accident/incident can be caused by small deviation from the normal process course, VisiMix® message system enables to define ISD/IST range of stirred reactors.

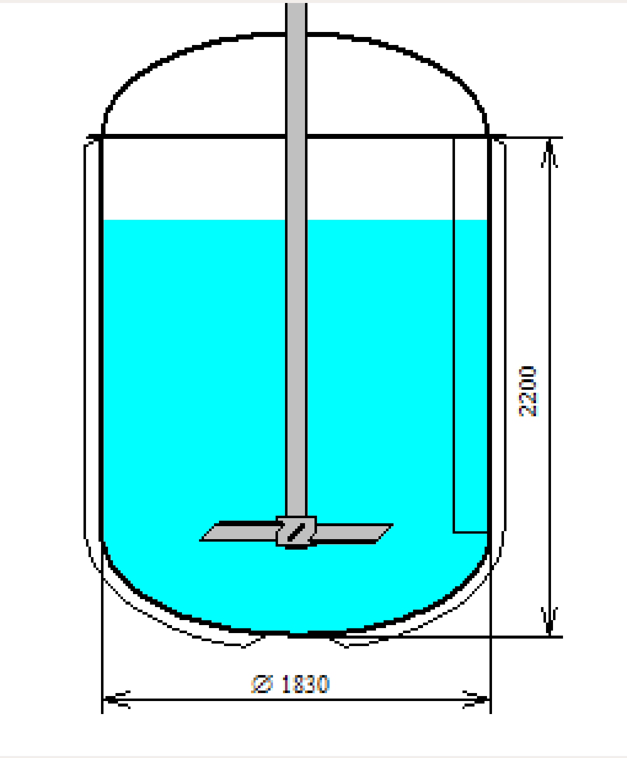
VisiMix® application in ISD/IST of chemical processes. *Example 1*:

Example 1. Tackling safety problems of stirred reactors at the *design stage*.

Problem Description. The actual process is performed in two stages:

1. **initial heating** which starts the reaction and
2. **subsequent cooling** required for removing excessive heat.

The heating is achieved by steam at atmospheric pressure supplied into the jacket, and the cooling is with ordinary water at 20°C circulated through the jacket. The considered process occurring in a cylindrical fully baffled stirred reactor is based on exothermal catalytic reaction involving solid catalyst. Analysis is performed aiming to define main process parameters and the process duration.



VisiMix® application in ISD/IST of chemical processes. *Example 1* (Cont'd)

From the safety standpoint this problem raises *two tasks* to be solved.

The ***first*** task is to provide Just Suspension Speed (***JSS***) – the minimum rotational velocity of the impeller at which there are no stagnant zones at the bottom.

The ***second*** task is to simulate a second order exothermal reaction in a stirred batch reactor aiming to avoid *runaway reaction* that takes place when the energy generated by the reaction is greater than the energy removed from the reactor. Kinetic reaction parameters were partially borrowed from the book *Safety, Health, and Loss Prevention in Chemical Processes. Problems for Undergraduate Engineering Curricula,* (The Center for Chemical Process Safety of the American Institute of Chemical Engineers) pp. 162 - 164, *Problem No. 81.*

VisiMix® application in ISD/IST of chemical processes.
Example 1 (Cont'd)

Problem Solution.

Task1. Choosing parameter **Complete/incomplete suspension** in the **Liquid-Solid Mixing** submenu results in warning messages informing the user of possible settling of solid particles every time when settling occurs.

Complete suspension is questionable

or

Partial settling of solid phase may occur

Thus the JSS is the minimum value of rotational velocity which does not result in the warning message. In our case JSS is equal to 72 RPM with a corresponding message.

Complete suspension is expected

VisiMix® application in ISD/IST of chemical processes. *Example 1* (Cont'd)

Problem Solution (cont'd).

Task 2. Heat transfer calculations performed for the *first* process stage (initial heating at first cause appearance of a warning message informing that at 443 sec (~7.3 min) a runaway reaction had started.

> After 443 sec have elapsed, the temperature falls outside the indicated range of process temperatures

Not that if instead of steam another heating agent Dowtherm SR-1 is selected the program will send the following warning message:

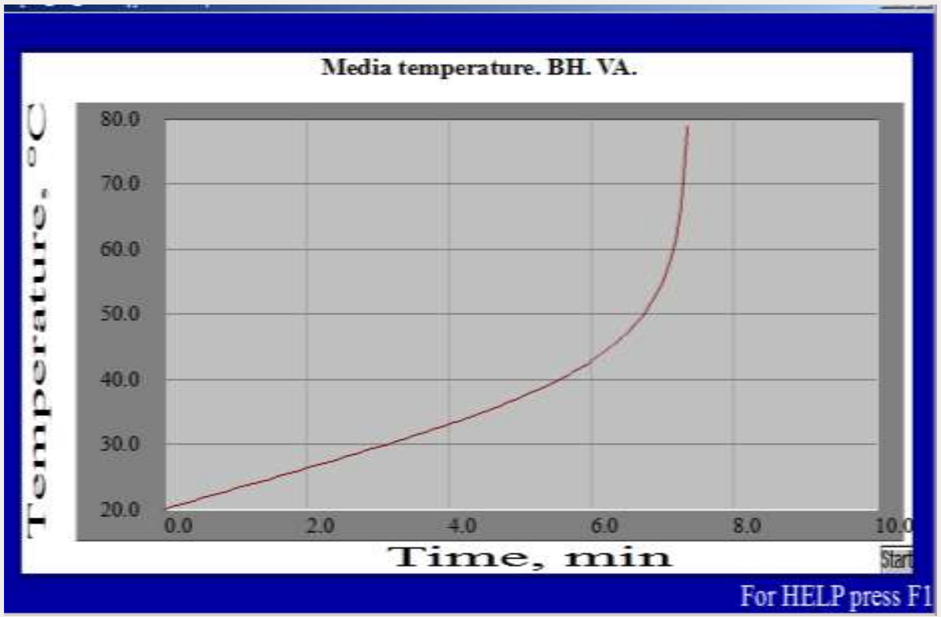
> ! This heat transfer agent doesn't correspond to process temperature range.

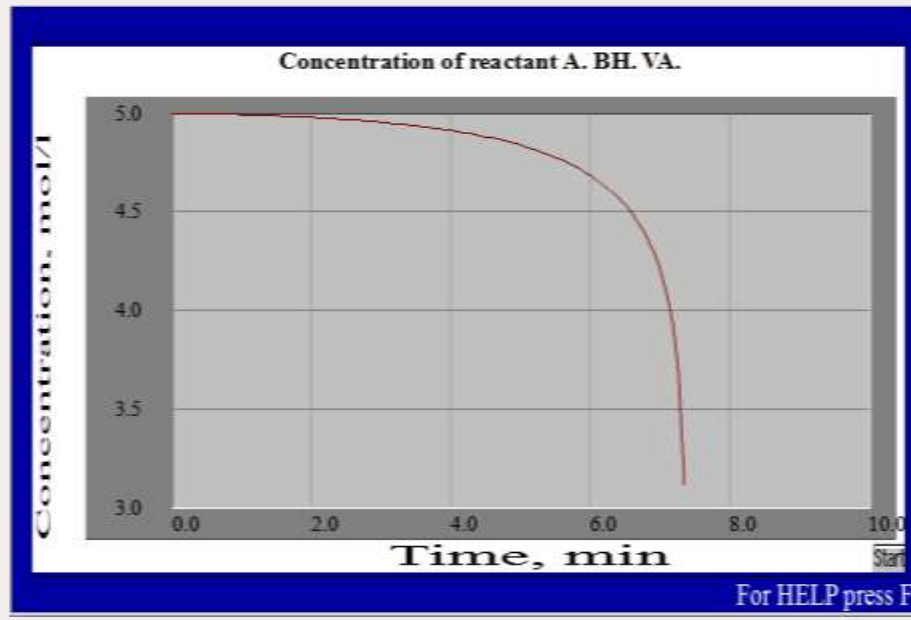
The reason is that an operating temperature of Dowtherm SR-1 is 121˚C that is less than the process upper temperature limit (143˚C).
It means that VisiMix® enables to avoid mistakes caused by a wrong selection of the cooling agent.

VisiMix® application in ISD/IST of chemical processes.
Example 1 (Cont'd)

Problem Solution (cont'd).

Media temperature and concentration history for the *first* process stage are presented below.



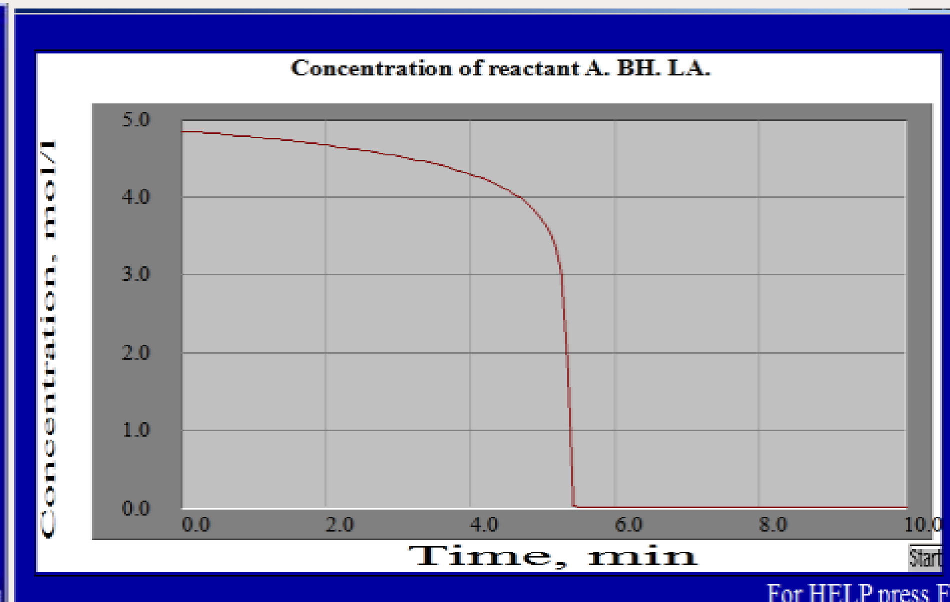


Based on these graphs the *first stage duration* is taken to be limited by 4.5 minutes from the start of the process and initial parameters of the second stage are 35°C and 4.85 mole/liter, respectively.

<u>VisiMix® application in ISD/IST of chemical processes.</u> <u>*Example 1*</u> (Cont'd)

Problem Solution (cont'd).

Results of the heat transfer calculations for the *second* stage with initial data defined in the previous slide are presented below



The duration of the cooling stage is about 5.3 minutes, and the total reaction time is about 10 minutes.

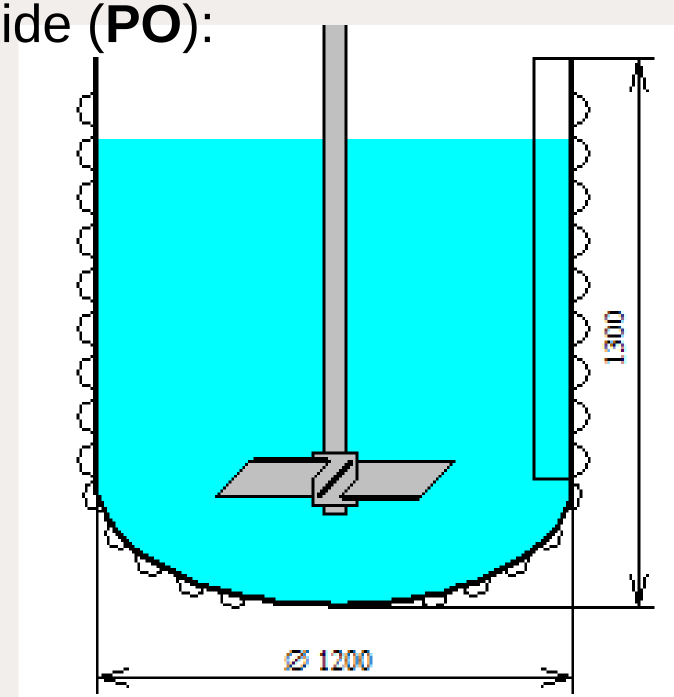
VisiMix® application in ISD/IST of chemical processes. ***Example 2***

Example 2. Tackling safety problems of stirred reactors during *operations*.

Process Description. This example taken from [H. Scott Fogler, *Elements of Chemical Reaction Engineering,* 2nd ed. (Prentice-Hall, Inc. (1992), pp.400 - 405, (*Examples 8-4 and 8-5*).] considers production propylene glycol (**PG**) by the hydrolysis of propylene oxide (**PO**):

$$PO + H_2O \xrightarrow{H_2SO_4} PG$$

This exothermal reaction takes place in a 300-gal reactor presented below at room temperature when catalyzed by sulfuric acid. The process has an important *operating constraint*. Because of the low boiling point of **PO** the temperature of the mixture inside the reactor must not exceed 130°F.



VisiMix® application in ISD/IST of chemical processes. *Example 2* **(Cont'd)**

Statement of the Problem.

1. Operation of any reactor over prolonged period causes a *fouling layer* in a tank jacket to grow that in turn will lead to increase of additional thermal resistance between in-tank media and in-jacket coolant. The last-mentioned affects the temperature regime inside the tank and may cause runaway reaction.
2. The fouling growth results in a *rise of the media temperature* which is usually compensated by increasing, accordingly, the *supply of coolant* into the jacket (the coolant flow rate and the corresponding *pressure head* on the jacket). The latter is usually used in control systems and corresponds to the VisiMix® parameter **Pressure head on the jacket**.

VisiMix® application in ISD/IST of chemical processes. *Example 2* (Cont'd)

Statement of the Problem (Cont'd).

3. Since the *capabilities of control systems are limited*, it is necessary to ensure the system to maintain the required pressure head in the considered case. Based on calculation results, the dependence of the **Relative Coolant Pressure Head** (on the jacket) on the **Fouling Thermal Resistance** ("*Safety Map*" for this process) was displayed graphically. The pressure head values used for this graph correspond to the minimum flow rate of the coolant at which the media temperature does not exceed the allowable limits.

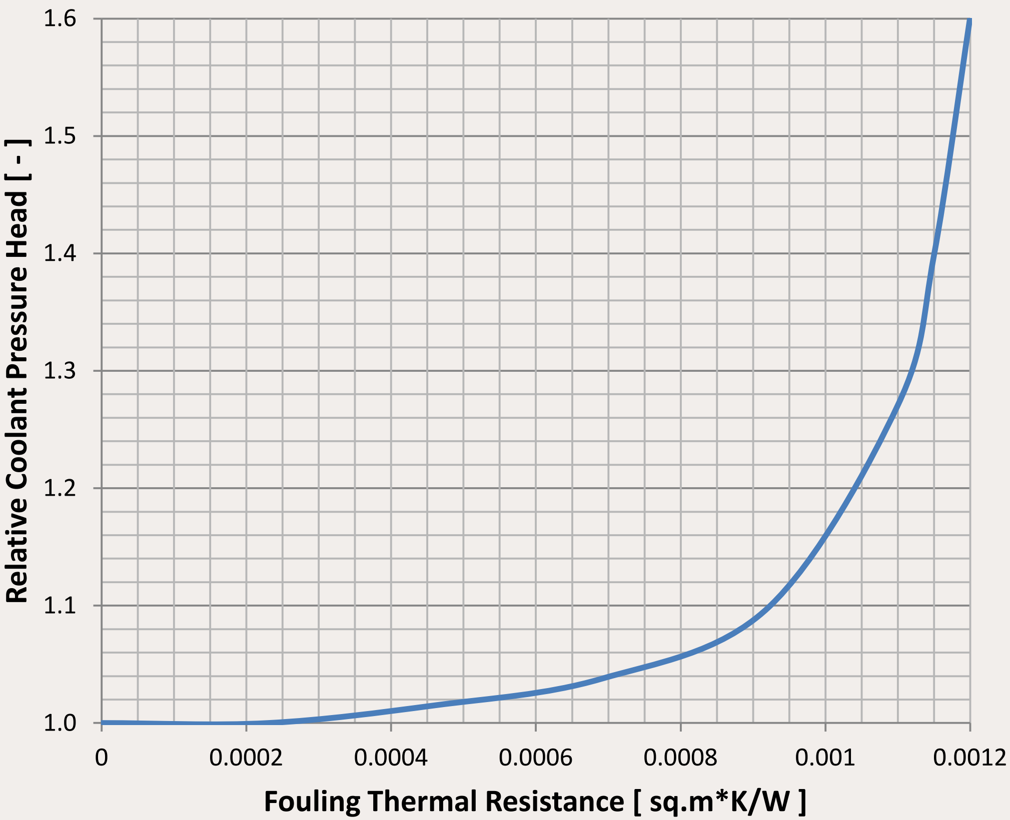
This Safety Map enables to check the ability of the control system to provide the required pressure head for compensating temperature rise caused by fouling.

VisiMix® application in ISD/IST of chemical processes. *Example 2* (Cont'd)

Safety Map

The Safety Map shows how the system is approaching the dangerous state when the control system is no longer capable of providing the required cooling and hence is setting the condition for the beginning of a runaway regime starting from the fouling thermal resistance ~0.001 m^2*K/W (for pure service water used as a coolant it corresponds to deposit layers with ~2mm thickness).

Thus the VisiMix® enables to define a criterion setting an upper limit for the process stoppage.

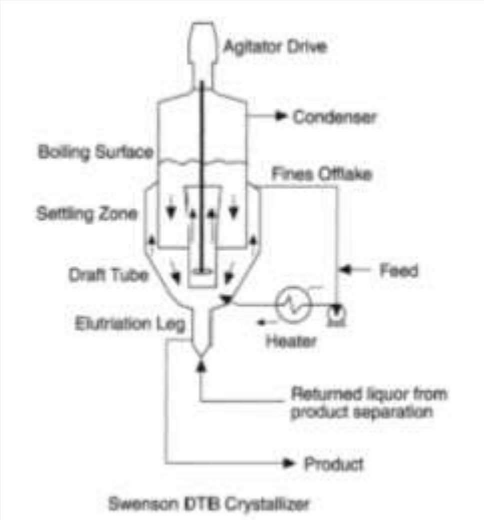


VisiMix® application in ISD/IST of chemical processes. *Example 3*

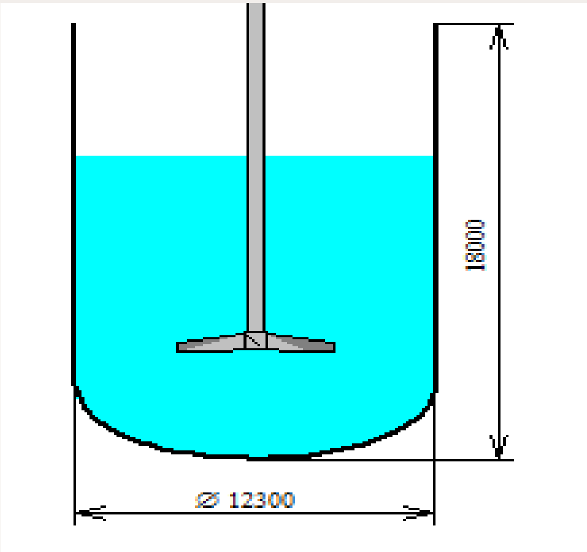
Example 3. Tackling safety problems in SRs: *incident/accident investigation.*

Incident Description. An incident took place in the crystallizer for the phosphoric acid production (its volume > 2000 m^3) equipped with a massive cast impeller with a tip diameter 5.33 m, and mass about 2000kg) and a draft tube. The crystallizer design is similar to the one depicted below at the left hand side. The incident starts shortly after the drive motor startup.

Crystallizer

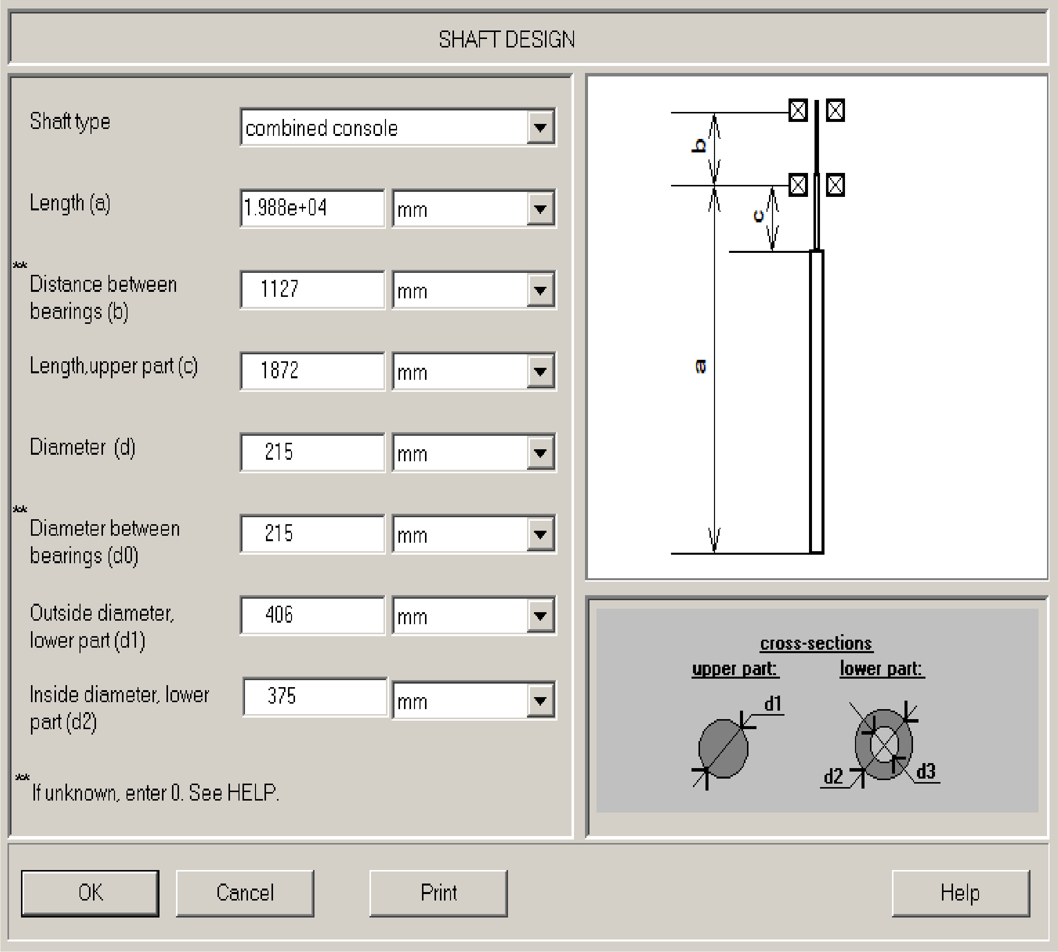


VisiMix® Model



VisiMix® application in ISD/IST of chemical processes. *Example 3* (Cont'd)

The VisiMix® model of the shaft is presented in the picture below.



VisiMix® application in ISD/IST of chemical processes. *Example 3* (Cont'd)

Analysis Results. As far as the problem under investigation is connected with the shaft breakage the VisiMix® submenu **Mechanical calculation of the shaft** was selected for the following study. This submenu enables to define **Torsion shear** and **Shaft vibration characteristics**. Any of them results in the following warning message.

> ⚠ Stiffness condition for shaft is not satisfied. See SHAFT VIBRATION CHARACTERISTICS

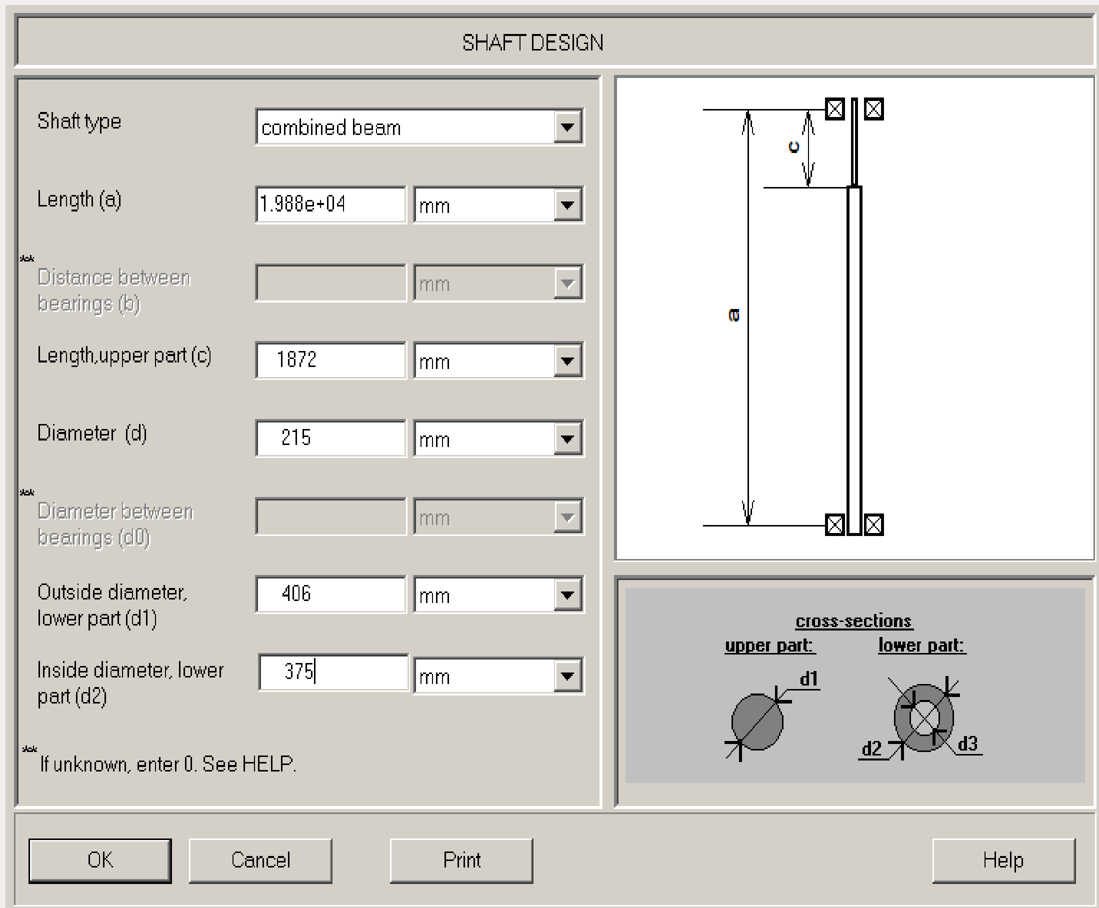
Checking **Shaft vibration characteristics** results is presented in the following table:

Parameter name	Units	Value
Critical frequency	1/s	0.309
Rotational frequency	Rps	0.412
Rotational to critical frequency ratio		1.33

The fact, that the shaft rotational frequency exceeds it critical value, means that after the massive impeller motor was switched on, the rotation speed increases gradually from the zero value up to the operation one. This start regime because of the impeller considerable mechanic inertia goes slowly and there is always a time interval when the shaft rotational frequency is close or equal to critical frequency that causes resonance oscillation with possible subsequent shaft breakage.

VisiMix® application in ISD/IST of chemical processes. *Example 3* (Cont'd)

Analysis Results (cont'd). A possible solution of the above problem is to increase the shaft stiffness. It can be achieved by replacement of the existing shaft with a mechanical scheme (combined console) with a new shaft with another mechanical scheme (combined beam) presented below.



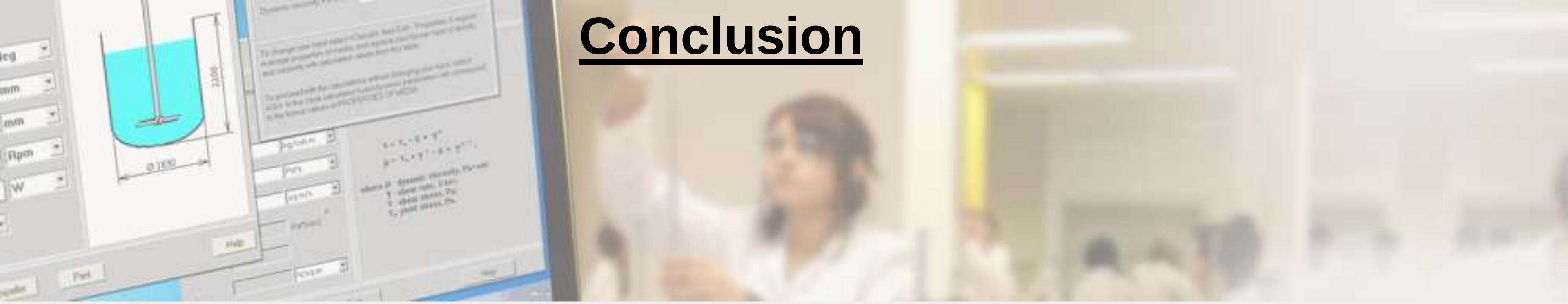
VisiMix® application in ISD/IST of chemical processes. *Example 3* (Cont'd)

Analysis Results (cont'd). Checking **Shaft vibration characteristics** results is presented in the following table.

SHAFT VIBRATION CHARACTERISTICS

Parameter name	Units	Value
Critical frequency	1/s	1.55
Rotational frequency	Rps	0.412
Rotational to critical frequency ratio		0.266

The table above conclusively demonstrates that the rotational frequency of the modified shaft is much below its critical frequency and thus the modified shaft design does not jeopardize appearance of the resonance oscillations.



Conclusion

An experience of the VisiMix® application enables to conclude the following:

1. Process analysis based on justified technical calculations and simulations is a mandatory element of the ISD/IST concept.
2. VisiMix® software has proven its capabilities in simulation various process in stirred tanks/reactors and estimation of their safety ranges (see www.visimix.com).

   It has the following features:

   - Provides adequate and complete simulation of the process and equipment configuration based on reliable models verified in practice.
   - Adequately detects any departures of the process course which are generally regarded as main factors causing accidents in the process industries and provide quantitative analysis of these factors influence.
   - It is user friendly, accessible to plant engineers and allows quick results.
   - Combines a calculation tool with an expert system that analyses initial data and calculation results, and warns the user whenever the system approaches dangerous operation regimes.

Conclusion (Cont'd)

3. A new version of the VisiMix® Turbulent tool will include an additional submenu specially adapted to ISD/IST problems and providing an engineer a list of tests corresponding to the considered unit operation (see table below) for revealing of possible sources of troubles.

<u>Conclusion</u> (Cont'd)

Unit Operations	List of ISD/IST Submenu Items/Tests
General mixing conditions	1. Inconsistency between drive power and mixing power
	2. Excessive vortex depth
	3. Dangerous proximity of shaft rotational velocity to critical frequency
	4. Inconsistency between shaft torque and strength limit.
Single-phase mixing	Danger of gas insertion from surface
Liquid – solid mixing	Inability of picking-up and distribution solid component
Liquid –liquid mixing	Inability of distribution of immiscible liquid
Gas-liquid mixing.	Inability of gas component distribution
Heat transfer process	1. Hazard of runaway reaction and overheating
	2. Inconsistency between selected heat transfer agent and process temperature range

Thus VisiMix® allows to predict dangerous situations and find technical means to mitigate/eliminate the probable risks. It means that VisiMix® usage provides stirred reactors a high degree of Inherently Safer quality.

Thank you !