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Accident States Simulation. Process Fluids Release

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Abstract: - Seveso II Directive imposes for high hazardous plants quantitative risk evaluation of the major accident. In a general context the risk is defined as product between frequency and consequences of accident state. There are five steps in quantitative risk assessment: identification of significant accident initiating events, development of accident sequences, frequency estimation for accident sequences, computation of post accident events parameters and consequences estimation. In the case of hazardous emissions, post accident events characterization means calculus of flow rates, quantities and duration. The paper presents mathematical models used to describe the process fluids release in emergency states, locally and by safety systems, as well as the results obtained with simulation programs, elaborated for the heavy water concentrations plants based on chemical exchange between water and hydrogen sulphide.

Key-Words: - Hazard, Risk, Release, Safety system, Simulation, Hydrogen sulphide, Mathematical model

1. Introduction

The legislation of European Community, especially Seveso II Directive, imposes upon the industrial producers more and more constrains regarding surveillance and control of pollution sources. These actions take aim the mitigation of the impact on peoples and environment, during the normal functioning of plants or in emergencies. Seveso II Directive imposes for high hazardous plants quantitative risk evaluation of the major accident.

Every production plant, that processes or storages hazardous materials, is equipped with safety systems. Some times their intervention can avoid transformation of incidents in accidents or can mitigate accident states consequences. Simulation calculus programs for process fluids release are useful tools in risk assessments and personnel training. They permit to calculate discharge flow rates, quantities of released hazardous materials and duration of release.

The paper presents mathematical models used to describe the process fluids release in emergency states, locally (by break) and by safety systems, as well as the results obtained with simulation programs. The simulation programs were elaborated for the heavy water concentrations plants that use the chemical exchange between water and hydrogen sulphide, called GS process.

2. Accidental process fluids release

All industrial plants that come under incidence of Seveso II Directive must elaborate safety reports, in order to demonstrate that they have a prevention policy of major accidents and safety systems management. This report must contain risk assessments, qualitative, semiqualitative or quantitative. In a general context the risk is defined as:

$$risk = frequency \times consequencies \qquad (1)$$

There are five steps in quantitative risk assessment:
- identification of significant accident initiating events,
- development of accident sequences,
- frequency estimation for accident sequences,

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- computation of post accident events parameters,

- consequences estimation.

For consequences assessment it is necessary to be known the quantity of hazardous materials released. When the accident does not involve destruction of the technological cover, the accident is controllable. Otherwise, depending on the safety systems states, the release is partial controllable or uncontrollable.

Romania built up an industrial heavy water platform, ROMAG-PROD Drobeta Turnu Severin, after experimentations carried out on a pilot plant, in Ramnicu Valcea Institute for Cryogenics and Isotopic Technologies. Therefore our preoccupations in industrial risk area refer to heavy water production. In Romanian, heavy water plants achieve the primary isotopic concentration by bithermal H_2O-H_2S chemical exchange (GS process) and the final one by vacuum water distillation. Figure 1 presents a schematic GS process unit.
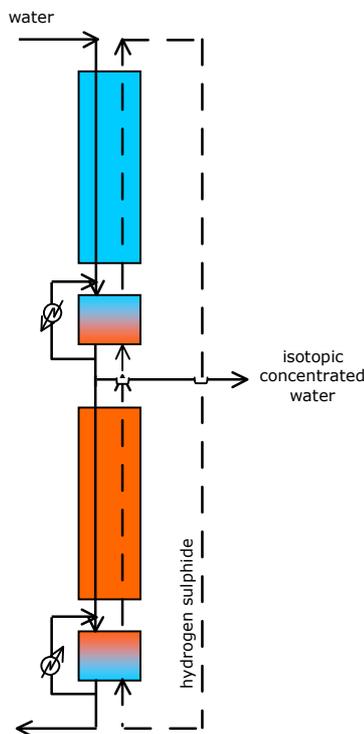

Figure 1 GS process unit

Figure 2, took from the ROMAG-PROD website, shows GS production lines [1].

In GS facilities are stored large quantities of hydrogen sulphide, a very high toxic, corrosive, flammable and explosive gas, maintained in process at relative high temperatures and pressures.

Fig. 2 View of the GS lines from
ROMAG-PROD Drobeta Turnu Severin

This fact imposed risk assessments, like for any chemical industrial activity. The most commune safety systems of these plants are: emergency stack, drainage system and water or nitrogen inundation system. Stages separation and interblocking systems are specific to multistage plants, and they are destined to create enclosures isolable automatically, as small as possible, like stages, stage sectors, equipment, pipe-line, etc.

Mathematical models and simulation software, elaborated on their basis, must ensure description of the process fluids discharge, locally and/or by safety systems. The process fluids contain hydrogen sulphide as aqueous solution, humid gas or liquefied gas.

Will be calculated and graphically presented the evolution in time of the release flow rates and system parameters, pressure and/or temperature.

3. Mathematical description

In isotopic concentration plants, based on H_2O-H_2S chemical exchange process, it produces hydrogen sulphide emissions during release of aqueous solutions, humid gas or liquefied gas. In order to describe these discharges one uses classical relation ships used in risk studies [2, 3, 4].

3.1 Calculus relations

During the adiabatic extension, one considers ideal behaviour for gas. The release flow rate from large vessels or pipes under pressure is calculated with the following calculus relation:

$$G_g = C_d \frac{A \cdot p}{c} \cdot Y \qquad (2)$$

where:

G_g - gas release flow rate (kg/s),
C_d - discharge coefficient,
A - break area (m^2),
c - sonic velocity of gas at vessel temperature,

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Y - flow factor,

Sound speed depends of the nature of material and temperature in breaking:

$$c = \sqrt{\frac{\gamma \cdot R \cdot T_b}{M}} \qquad (3)$$

$$\gamma = \frac{C_p}{C_v} \qquad (4)$$

$$C_p - C_v = R \qquad (5)$$

where:

γ - specific heats ratio

R – gas constant

T_b – temperature in breaking (K)

T – inside temperature (K)

M – gas molar mass (kg/kmol)

C_p - molar specific heats at constant pressure

C_v - molar specific heats at constant volume

For an ideal gas, the temperature in breaking one calculates:

$$\frac{T_b}{T} = \frac{2}{\gamma - 1} \qquad (6)$$

For humid gas the molar specific heat one calculates /2/:

$$C_p = C_{p_{H_2S}} \cdot \frac{1}{u+1} + C_{p_{H_2O}} \cdot \frac{u}{u+1} \qquad (7)$$

where:

C_p - molar specific heats at constant pressure of the humid gas, (cal/mol³ grd)

$C_{p_{H_2S}}$ - molar specific heats at constant pressure of H_2S, (cal/mol³ grd)

$C_{p_{H_2O}}$ - molar specific heat at constant pressure of steam, (cal/mol³ grd)

C_v - molar specific heats at constant volume of humid gas, (cal/mol³ grd)

u - gas humidity

There are possible two flow regimes, subsonic and sonic, depending of the critical value of pressures ratio:

$$r_{cr} = \left(\frac{p}{p_a}\right)_{cr} = \left[\frac{\gamma - 1}{2}\right]^{\frac{\gamma}{\gamma - 1}} \qquad (8)$$

where:

p - storage pressure (N/m²),

p_a - ambient pressure (N/m²),

The regime is subsonic or sonic if the momentary value of pressures ratio is less then critical ratio (r_{cr}), or equal or higher then this one. Flow rate factor depends on the flow pattern:

- subsonic flow $\left(p/p_a < r_{cr}\right)$

$$Y = \frac{2 \cdot \gamma^2}{\gamma - 1} \cdot \left(\frac{pa}{p}\right)^{\frac{2}{\gamma}} \cdot \left[1 - \left(\frac{pa}{p}\right)^{\frac{\gamma - 1}{\gamma}}\right] \qquad (10)$$

- sonic flow $\left(p/p_a > r_{cr}\right)$

$$Y = \gamma \cdot \left(\frac{2}{\gamma - 1}\right)^{\frac{\gamma + 1}{2 \cdot (\gamma - 1)}} \qquad (11)$$

Liquid flow rate is calculated with Bernoulli relation:

$$G_l = C_d \cdot A \cdot \rho_l \cdot \sqrt{2 \cdot \frac{p - p_a}{\rho_l} + 2 \cdot g \cdot h} \qquad (12)$$

where:

G_l – liquid release rate (kg/s),

ρ_l - liquid density (kg/m³),

g - gravity constant (m²/s),

h - liquid head above hole (m).

Gas desorption flow rate from released process water is determined using H_2S solubility:

$$G_{des} = G_l \cdot \frac{S}{1 + S} \qquad (13)$$

where:

G_{des} – gas desorption flow rate (kg/s),

Ș- gas solubility in water (kmol H_2S / kmol H_2O),

Gas solubility in water depends on temperature and pressure [6].

If the liquefied gas releases by a relative small diameter break the release flow rate calculates with Bernoulli equation (12). When the liquefied gas releases by a break of relative large diameter then a biphasic flow occurs.

$$G_m = C_d \cdot A \cdot \sqrt{2 \frac{p - p_a}{v_m}} \qquad (14)$$

where:

G_m – biphasic release rate (kg/s),

v_m - specific volume of mixture (m³/kg),

One assumes that those two phases form a homogenous mixture, in equilibrium state. The rate of evaporated liquid, at critique value of flow rates ratio, is:

$$f_{vm} = \frac{C_{pl} \cdot \left(T_l - T_{s,c}\right)}{H_{lv,c}} \qquad (15)$$

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where:

C_{pl} = liquid specific heat (kJ/(kg.K))

T_l = liquid temperature (K)

$T_{s,c}$ = saturated vapour temperature at critical pressure (p*) in orifice (K)

$H_{lv,c}$ = vaporization heat at critical pressure in orifice (kJ/kg).

Fast depressurization of H_2S liquefied storage vessel leads to an abrupt decrease of the temperature (Joule-Thomson effect) and endangers the mechanical strength of vessel. In order to calculate temperature decrease one uses Joule – Thomson coefficient,

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = \frac{T\left(\frac{\partial v}{\partial T}\right)_P - v}{C_P} \qquad (16)$$

Redlich Kwong equation of state,

$$\frac{P \cdot v}{R \cdot T} = \frac{v}{v - b} - \frac{a}{RT^{3/2} \cdot (v + b))} \qquad (17)$$

and a relationship to calculate saturated vapour pressure, as a function of temperature [5].

$$P = f(T) \qquad (18)$$

The release time one determines from the unsteady state mass balance:

$$[entrances] - [exits] = [accumulation],$$

described by a differential equation:

$$-G = \frac{d\,m_i}{d\,t} \qquad (19)$$

where:

m – enclosure hold-up (kg),

t - time (s).

When in the equipment two phases co-exist, m_i refers only to the releasing phase.

Calculus of the isolable enclosure hold-up presumes detailed knowledge about dimensions of the facilities, operation procedures and functioning parameters.

Non-linearity of the presented equations imposed the adoption a numerical method to solve mathematical models [7].

The system pressure is recalculated, at each iteration, considering that during gas and/or process water discharges the temperature remain constant and the gas have ideal behaviour.

For each accident scenario it takes into consideration the possibility of human intervention. The start of some safety systems is not automatic,

waiting the techno log decision. The calculus programs ask the time after that safety systems start.

Results obtained by simulation programs are presented automatically by tables and diagrams. The tables show entrance data and values of the main discharge parameters. The diagrams present the evolution in time of the calculated variable parameters. In this paper the calculus results are presented by diagrams.

3.2 Applications

The presented relations have general availability but the mathematical models constructed with them and simulation programs are specifically to an application.

The GS isotopic concentration plant is equipped with classical safety systems:

- emergency stack for rapid gas discharge and burning at high distance from ground level

- inundation system, to maintain with clear water the liquid level above the break.

Hydrogen sulphide storage plant is equipped with drainage system for quick liquefied gas transfer into an other storage vessel, emergency stack and nitrogen inundation system.

The accident scenarios with process fluids release, for that we have elaborated simulation programs, are:

1 – fissure/ break of GS plant equipment, in space filled with gas

2 – fissure/ break of GS plant equipment, in space filled with process water

3 – fissure/ break of H_2S storage plant equipment in space filled with H_2S vapour

4 – fissure/ break of H_2S storage plant equipment, in space filled with liquefied gas.

During accident scenario us no. 1 and no. 3 it can be two discharge fluxes;

- by break (local discharge)
- by emergency stack.

Three simultaneous discharge fluxes can appear during accident scenarious no. 2 and no. 4:

- liquid or gas by break (local discharge)
- gas by emergency stack
- liquid by drainage system.

On the basis of these four kinds of accident scenarios, in the frame of a national project, our institute realized calculus programmes to characterize fourteen specific emergency situations [7].

The paper presents calculus models and simulation results for accident scenario 2 and 4.

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Depending on the events development, in the case of scenario 2 and 4 it can find also events from accident scenario 1, 3 respectively.

3.2.1 Scenario 2

Depending on the type of damaged equipment, the interventions in case of fissure/break occurrence in liquid area of GS plants are of two types, as well as mathematical models.

a) column or pipe unisolated from the column

One activates the isolating systems, for stages isolation and interblocking, one starts water inundation and gas discharge to emergency stack. Mathematical model for process fluids discharge simulation is formed of the:

- equation for local (by fissure / break) release of liquid

$$(12)$$

- equations for gas release by emergency stack

$$(2),(3), (4), (5), (6), (7), (8), (9), (10)/(11)$$

- equation for local gas discharge, produced when the liquid level decreases under break level

$$(2)$$

- equation for global mass balance

$$(19)$$

The gas evacuation to emergency stack it realizes in two stages, by diaphragms of different diameters $(d_1 < d_2)$.

b) pipe-line

One activates the isolating systems and starts process water drainage. Mathematical model for simulation process fluid discharge is formed of the:

- equation for local liquid release

$$(12)$$

- equation for liquid drainage

$$(12)$$

- equation for global mass balance

$$(19)$$

For accident scenario 2 one simulates process fluids discharge by a 120 mm break, issued in the H_2O – H_2S exchange column (d=5.3m). Two minutes after event occurrence it begins inundation from a high pressure water pipe-line and after 3 minutes gas discharge by emergency stack. Evolutions in time of the discharge flow rates, as well as water inundation flow rate are presented in figure 1a. Figures 1b and 1c present variation of the liquid level above break and inside column pressure. Analyzing these diagrams it can observe the necessity to begin inundation in a short time after event occurrence, otherwise liquid level can go down, under break and one produces H_2S gas discharge. When the liquid level attaints ~ 40 m one closes water admission. This initial level assures during gas evacuation to emergency stack the break obturation. Figures 2a, 2b and 2c present H_2S release flow rates, by desorption from process water, local and at stack.

3.2.2 Scenario 4

When a fissure / break occurs in liquefied gas storage vessel, under liquid level, one activates liquid transfer (drainage) in emergency reservoir and gas discharge to emergency stack. The mathematical model for simulation the liquefied gas discharge consists of:

- equations for local liquefied gas discharge

$$(12) \text{ or } (13), (14), (15)$$
$$(16), (17), (18)$$

- equations for liquefied gas discharge by drainage system:

$$(12) \text{ or } (13), (14), (15)$$
$$(16), (17), (18)$$

- equations for gas release by emergency stack

$$(2),(3), (4), (5), (6), (7), (8), (9), (10)/(11)$$

- equation for global mass balance

$$(19)$$

Like at scenario 2, the gas evacuation to emergency stack it realizes in two stages.

For accident scenario 4 one simulates liquefied H_2S discharge by a break of 10 mm, situated at the bottom of storage vessel (d=1 m). After 1 minute from event occurrence one activates gas evacuation to emergency stack and after 2 minutes liquid drainage to emergency storage vessel. The diagrams from figures 3a, 3b and 3c present evolution in time of the liquefied gas discharge flow rates, local and by drainage system, liquid level above break and inside temperature. Inside pressure and discharge flow rates, local and at emergency stack, are presented in figures 4a, 4b and 4c. Rapid pressure decrease produces accentuated temperature decrease. In order to maintain the temperature level above -30°C, one admits a depressurization just to 3 bar. Cooling under this value can affect mechanical resistance of the vessel.

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4. Conclusions

The paper presents mathematical models used to describe process fluids release in accident situations, local and by safety systems, as well as the results obtained with simulation programs elaborated for isotopic concentration plants, that used $H_2O - H_2S$ chemical exchange process.

Simulation programs elaborated in our institute were installed and tested to Romanian industrial heavy water producer, ROMAG-PROD Drobeta Turnu Severin. Fortunately there are data just for comparing with gas discharge by emergency stack. It was obtained a good prediction for this manoeuvre.

The simulation programs for process fluids discharge in emergency situations are useful in risk assessment and for personnel training.

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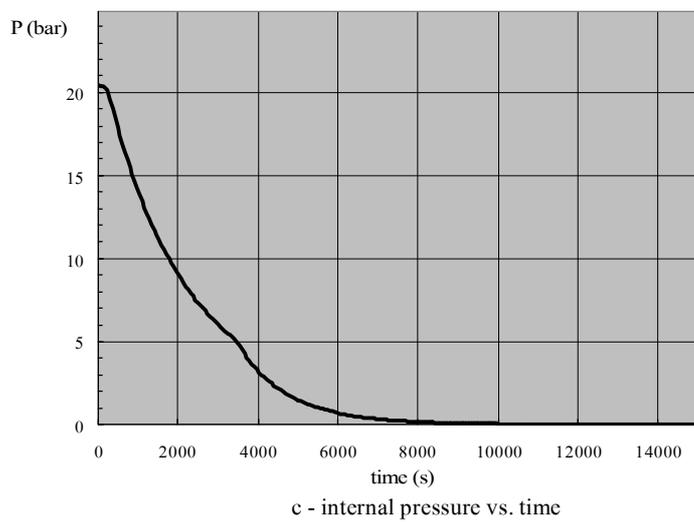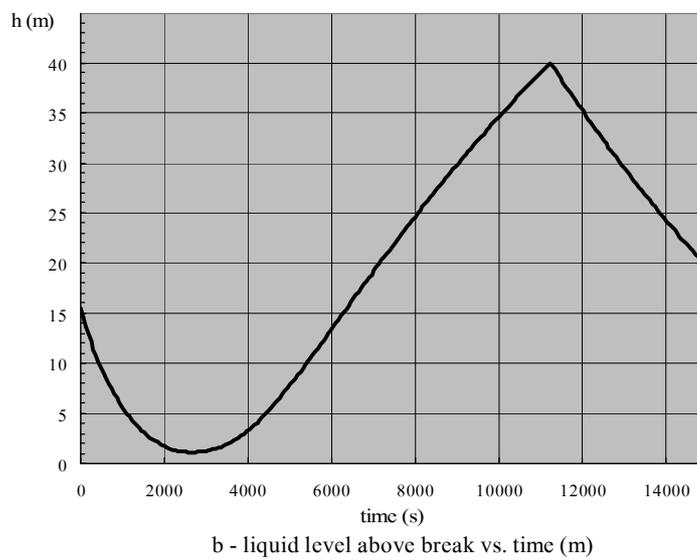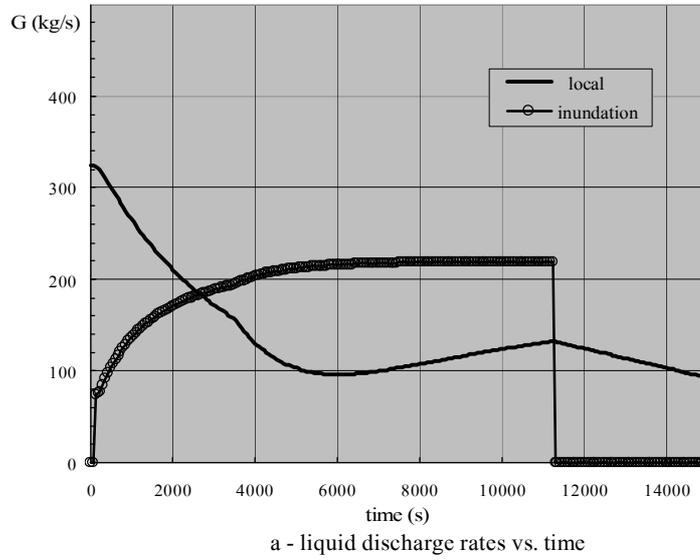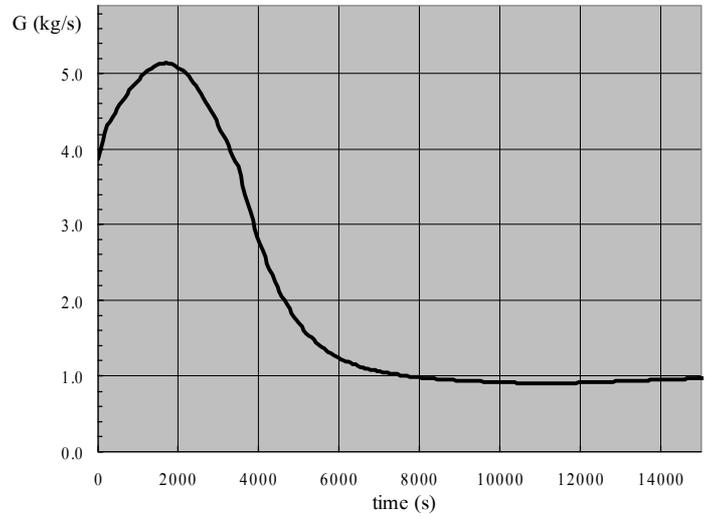
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a - liquid discharge rates vs. time

b - liquid level above break vs. time (m)

c - internal pressure vs. time

Figure 1

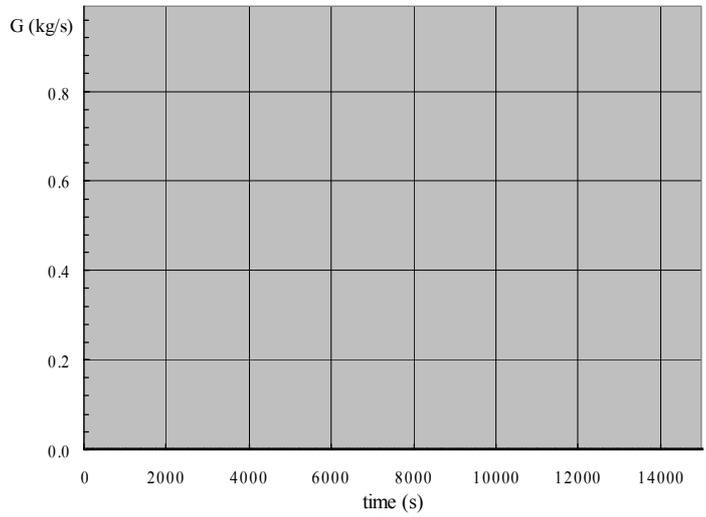Cornelia Croitoru, Mihai Anghel, Floarea Pop, Ioan Stefanescu, Gheorghe Titescu, Mihai Patrascu, Ervin Watzlawek, Dorin Cheresdi

c - local gas desorbtion rate vs. time

b - local gas discharge rate vs. time
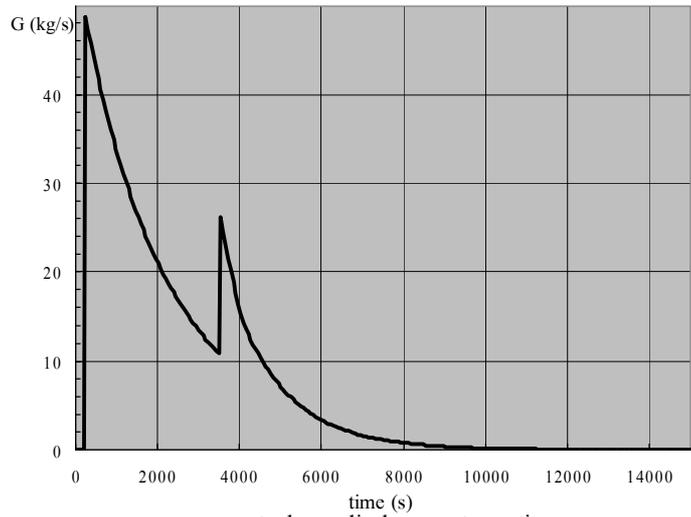
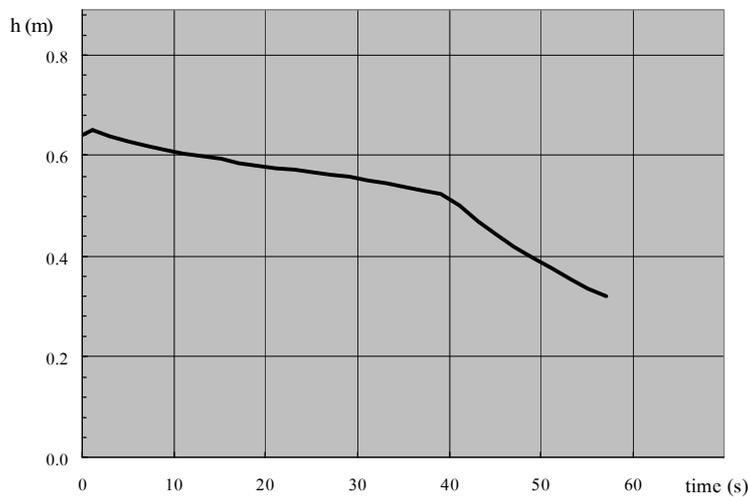a - stack gas discharge rate vs. time

Figure 2

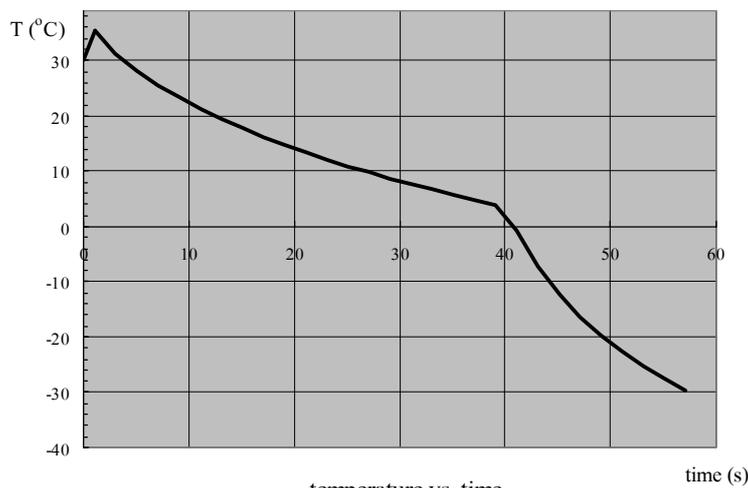Cornelia Croitoru, Mihai Anghel, Floarea Pop, Ioan Stefanescu, Gheorghe Titescu, Mihai Patrascu, Ervin Watzlawek, Dorin Cheresdi
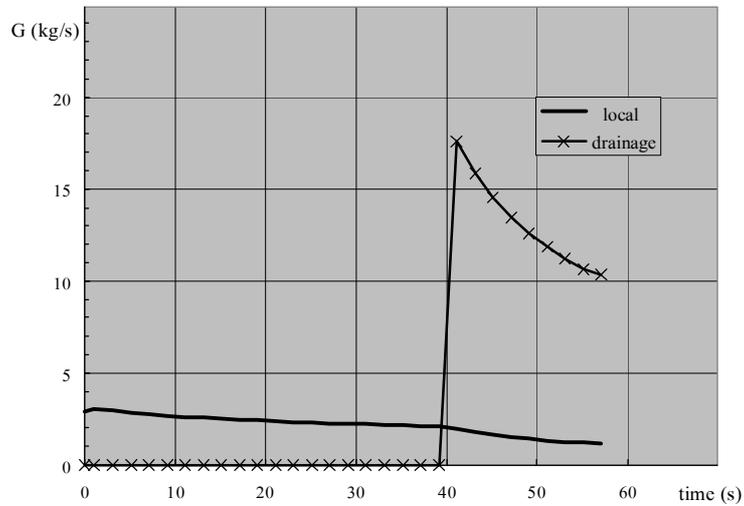
liquefied gas release rate vs. time

liquid level above break vs. time (m)

temperature vs. time

Figure 3

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inside pressure vs. time

local gas discharge flow rate vs. time

stack discharge flow rate vs. time

Figure 4