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Systematic Approach for Assessing the Safety Measures for Reaction Vessels

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ABSTRACT: This is a short report about the study „Requirements of technical equipment at reaction vessels to avoid emissions of dangerous substances via pressure-relief systems“. The study shows how the hazards involved can be systematically analyzed, and the requirements of the safety measures can be defined and documented. The evaluation of the 41 mainly batch-processed reaction vessels of the Bavarian chemical industry showed that the emission of substances is prevented above all by process-control measures. The reaction vessels are generally equipped with pressure-relieving systems, because they also limit the extent of the damage in case of a failure.

1 INRODUCTION

In 1993 a series of major-accidents at the Hoechst factories drew the attention of the German public to the safety of reaction vessels. In Frankfurt-Griesheim an unacceptable overpressure built up in a reaction vessel for the production of ortho-Nitroanisol. When the safety valves of the reaction vessel opened at about four o'clock in the morning about 10 tons of mixed chemical substances escaped into the atmosphere and came down as a yellow rain around Schwanheim and Goldstein.

It is not unusual for accidents initiated by runaway reactions to be accompanied by severe and irreversible consequences. What we have learned from the causes in past accidents is as follows:

- little knowledge of the process chemistry;
- poor evaluations and reviews;
- incorrect operational procedures;
- lack of mixing;
- low quality of reactants;
- safety critical modifications that are insufficiently hazard studied or not documented;
- inadequate reactor maintenance;
- insufficient reactor operating instructions, procedures and training.

2 STUDY

As a result of the accident at Hoechst in 1993 the Bavarian State Ministry of Environmental Protection placed an order with TÜV to carry out a study on the following subject:

> *Requirements of technical equipment at reaction vessels to avoid emissions of dangerous substances via pressure-relief systems.*

The study was based on the inspection of 41 reaction vessels in the Bavarian chemical industry. The study was made, discussed and published together with the Ministry and the Bavarian Chemical plants (Association of chemical industry, VCI).

The study shows how the hazards involved can be systematically analyzed, and the requirements of the safety measures can be defined and documented.

The systematic approach described in a specific decision-making diagram gives us the following advantages and fulfills the following general requirements:

- Individual solutions
- Risk-orientated fixing of safety measures
- Practice-orientated help
- Transparency and plausibility of the decision-making process in an individual case
- Pre-existing and approved facts as a basis

2.1 Safety equipment of reaction vessels

2.1.1 Process-control systems

The task of a safety instrumented system is to prevent an impermissible fault state of the process plant. In the event of an unacceptable situation an automatic shutdown is triggered, or the permanently-present operating personnel alerted by an alarm signal carry out necessary and previously well-defined countermeasures. In all cases, the functions of a safety instrumented system override the functions of basic process-control systems and process-control monitoring systems.

In contrast to the functions of a basic control system, the functions of safety instrumented systems are rarely demanded. Within the context of Seveso-II safety instrumented systems are significant as safety measures for the prevention of major-accidents. When estimating the risk to be covered by safety instrumented systems, the risk without the existence of the safety instrumented system under consideration is to be assumed.

The risk can be systematically and verifiably determined using the method detailed in DIN V 19250 or VDI/VDE 2180 (see today also draft IEC 61511[1]). Following this standard the requirement classes for the process-control protective measures are found with the help of almost entirely objective parameters. As a rule, the higher the number of a requirement class, the larger the part-risk to

[1] Functional safety of Safety Instrumented Systems for the Process Industry Sector - Informative; Part 3: Guidance for the determination of safety integrity levels - infromative

be covered by the safety instrumented system and therefore generally the more stringent the requirements and resulting measures. In the special case of reaction vessels, requirement classes 7 and 8 are not covered by safety instrumented systems alone. Non-process-control measures are needed to reduce the risk to at least requirement class 6.

To avoid faults and ensure control and therefore achieve higher availability with regard to safety, special technical and organisational measures are to be taken for safety instrumented systems.

2.1.2 Pressure-relieving devices

If an unacceptable pressure increase is possible and if this can result in blowing off the pressure-relieving device, a risk-free discharge must be ensured. With the help of a dispersion assessment the immission concentrations in the atmosphere after blowing off the pressure-relieving device can be calculated and evaluated. If risk-free discharge can not be guaranteed by a dispersion assessment, further safety measures are necessary, for example suitable blow-down and disposal systems will be required.

The evaluation of the 41 mainly batch-processed reaction vessels of the Bavarian chemistry industry showed that the emission of substances is prevented above all by process-control measures. The reaction vessels are generally equipped with pressure-relieving systems, because they also limit the extent of the damage in case of a failure (for example maximum extent of damage: the reaction vessel bursts).

The use of blow-down and disposal systems remains an exception only with great risks with critical substances or reactions. Compared with blow-down and disposal systems the process-control measures offer the advantage that in case of a failure or fault measures can be taken directly and effectively and the development of critical situations can be prevented from the beginning.

2.2 Hazard identification and risk assessment

Hazard identification and risk assessment are particularly important and are best carried out by a team of qualified people whose members have a range of skills, technical knowledge gained from safety inspections or from the operation of reaction vessels.

Hazard identification is a crucial step in the systematic approach. Risk assessment is essential to evaluate the likelihood of a fault and the severity of its potential consequences. The extent of risk analysis and the intensity of the safety measures should correspond with the risk involved.

A specific decision about a safe process and the necessary safety measures has to be made in each individual case. It is the task of the team of experts to use their technical knowledge within the context of the decision-making diagram to find a suitable solution to the particular problem.

The general procedure in the decision-making diagram is as follows and can be described in four steps. For each step an own list exists:

1. ***Chemical substances***

The first question is whether there are substances involved which present a potential hazard. The list 1 "Evaluation of the substances hazard potential" helps to determine whether the substances involved present a potential hazard.

2. ***Hazard identification***

A thorough and extensive analysis of the process involved is necessary (safety review) whether plant safety is based on pressure-relieving devices and/or process-control safety measures. This must include consideration of the fact that process steps may deviate from the specified operating conditions.

List 2 is a kind of checklist which already includes many of the faults possible in connection with reaction vessels, which might lead to an unacceptable increase in pressure. With the help of the list it must be examined if a major-accident caused by a fault might happen or not. Furthermore it is also tested if the pressure-relieving device is suitable for such an event. Additionally, the risk parameter "probability of occurrence" is evaluated in line with the requirements outlined in DIN V 19250.

3. ***Dispersion assessment***

The following list 3 serves to evaluate the risk-free discharge from a pressure-relieving device and/or to determine the risk parameter "extent of damage" (DIN V 19250). For this purpose the potential faults, worked out from aforementioned list 2 are listed once again. In general, there are far fewer faults than originally listed and examined in list 2. For these remaining faults it is necessary to determine or estimate the amount of the relevant substance released per time unit.

4. ***Requirement class (Risk assessment)***

If a safety instrument system is provided, we will now have almost all the data necessary for the definition of the requirement class (or SIL according to 61511-3). List 4 which lists the potential faults and defines the appropriate safety measures serves for this purpose. Two risk parameter are defined (list 2: probability of occurence; list 3: extent of damage). Now, two more risk parameters remain to be clarified. The "duration of stay" and the "hazard prevention". The requirement class for the safety instrument system can thus be derived from the risk chart (see Figure 1).

Through the use of the systematic approach developed in the study highly individual, intelligent and risk-oriented solutions become transparent and plausible. It shows a possibility to meet the requirements of Seveso-II-directive in a safety report.

The decision-making diagram and lists developed during this study allow logical documentation of the solutions. It can demonstrate that major-accident hazards have been identified and that the necessary measures have been taken to prevent such accidents and to limit their consequences for man and the environment. It enables clear delineation in planning, erection and operation and also during subsequent modifications.

The use of possibly simpler, clearer and directly-acting measures usually leads to safe solutions which are also more economical.

SÜDDEUTSCHLAND

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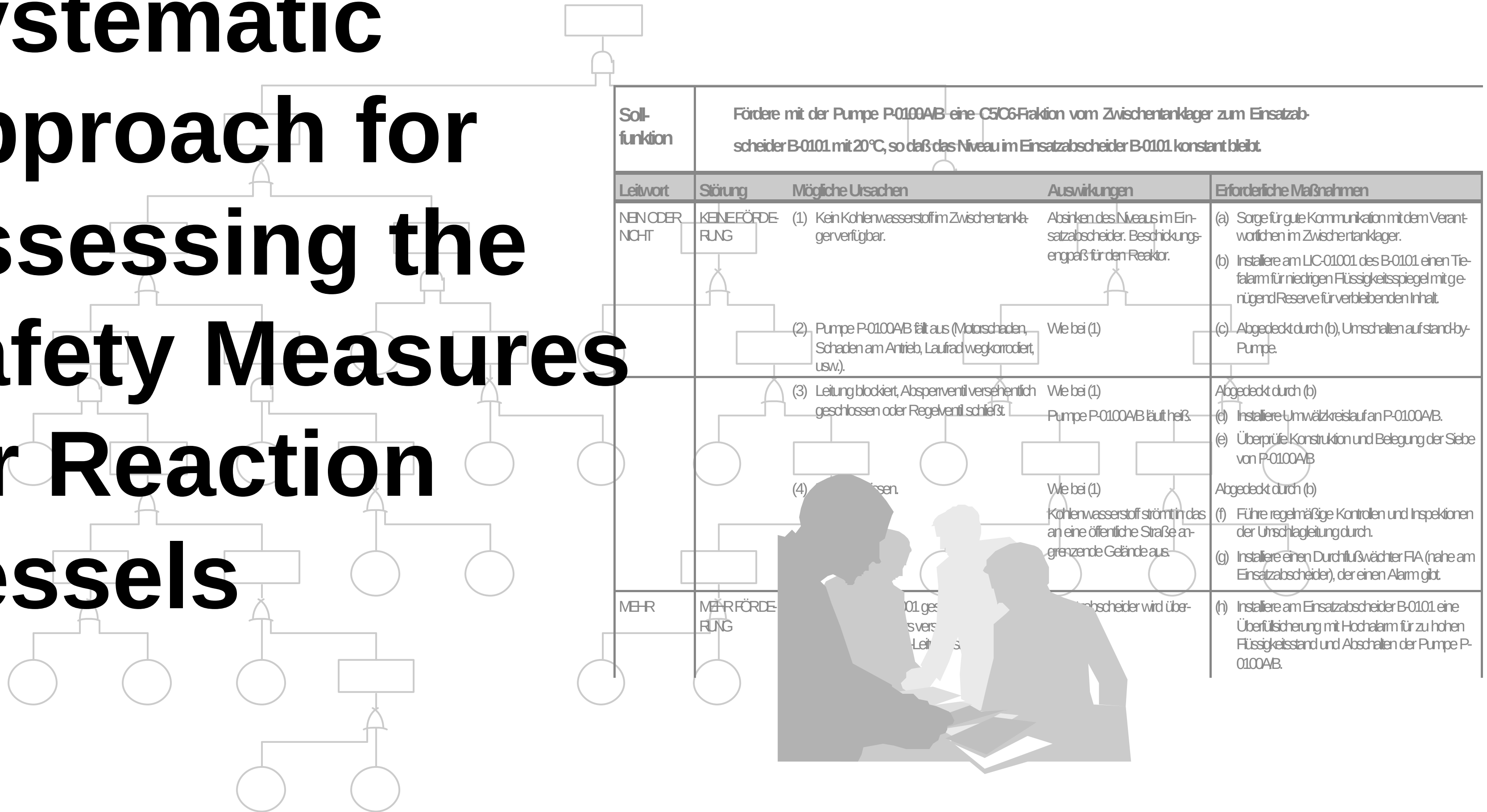

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Seveso-II-Directive (96/82/EC)

Article 9: Safety report

1. Member States shall require the operator to produce a safety report for the purposes of:

.....

b) demonstrating that major-accident hazards have been identified and that the necessary measures have been taken

- to prevent such accidents and
- to limit their consequences for man and environment;

.....

Systematic Approaches

Identification

Checklists
Substance tolerances

Failure mode and effect analysis (FMEA)

Operating error analysis

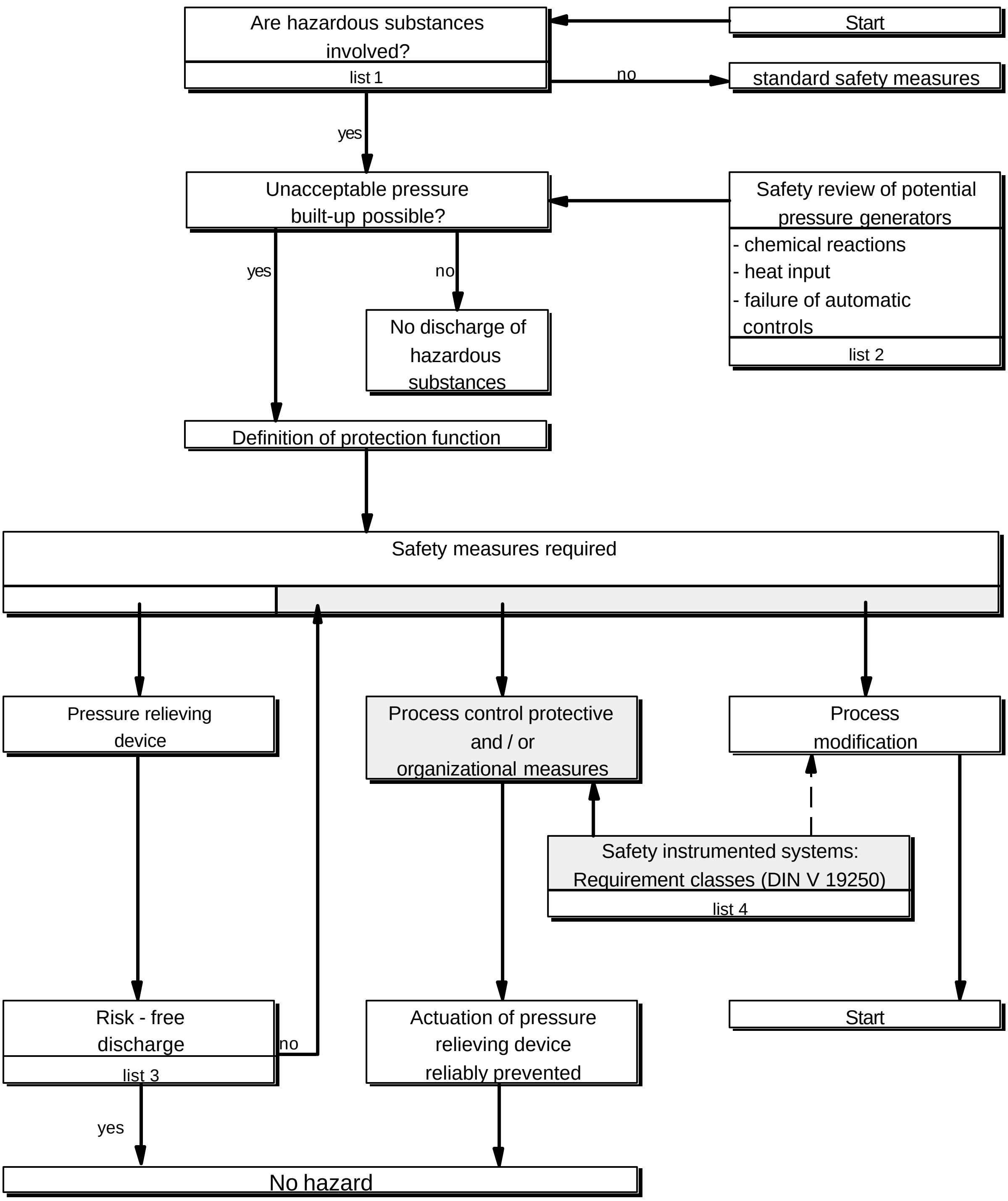
HAZOP / PAAG

Evaluations

<u>Quantitative methods</u>
Probability
 Event tree analysis
 Fault tree analysis
Extent of damage

<u>Semi-quantitative methods</u>
Index methods
Zurich hazard analysis
Risk chart according to DIN V 19250, VDI/VDE 2180 or IEC 61508/61511

Decision-making Diagram



Example

1. Chemical Substances

- Reactant A: 2300 kg, gaseous, hazardous properties: F
- Material B (trace in A): gaseous, hazardous properties: T, F
- Reactant C: 850 kg, liquid, hazardous properties: T, C
- Catalysator D: 17 kg, gaseous, hazardous properties: T+, C

Reaction Enthalpy: 48 kJ/mol A

Max. Pressure: 6 bar

Max. Temperature: 120 °C

Example

2. Hazard identification:

• Accumulation of reactants	W 1
• Agitator failure	W 2
• Breakdown cooling	W 2
• Overheating	W 1
• Overfilling	W 1

Example

3. Dispersion assessment

- Accumulation of reactants
  (max. 1197 kg A) S 3
- Agitator failure
  (max. 1,25 kg A/s, max. 100 g D) S 2
- Breakdown cooling (see Agitator failure) S 2
- Overheating (see Agitator failure) S 2
- Overfilling (max. 60 g A, risk-free discharge) S 1

Risk parameter - I

Extent of damage

S1: Slight injury to a person; damaging environmental effects

S2: Serious irreversible injury to one or more persons, death of a person or temporary, severe harmful environmental influences

S3: Death of several persons or long persistent, serious, harmful environmental effects

S4: Catastrophic effect, very many dead

Risk parameter - II

Probability of occurence

W1: Very low

W2: Low

W3: Relatively high

Duration of stay

A1: Seldom to often

A2: Frequently to permanently

Hazard prevention

G1: Possible under certain conditions

G2: Barely possible

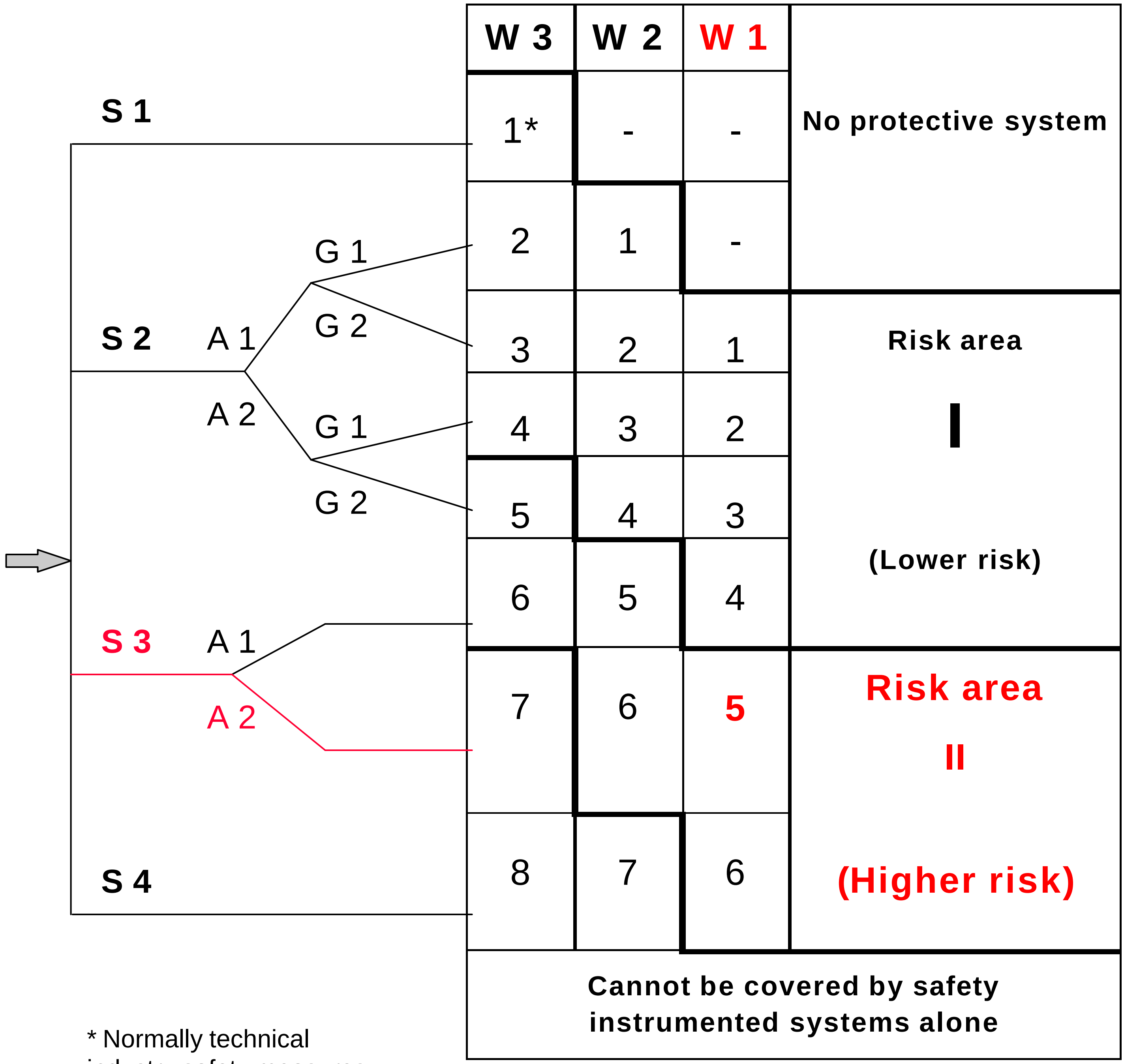
Example

4. Risk assessment

		Risk parameter				
		Extent of damage	Probability of occu-rence	Duration of stay	Hazard preven-tion	Require-ment class
Accumulation of reactants	TIRCZ-A-	S3	W1	A2	-	5
Agitator failure	SZ-A-	S2	W2	A2	G1	3
Breakdown cooling	TIRCZ+A+	S2	W2	A2	G1	3
Overheating	TIRCZ+A+ PIRS+A+	S2	W1	A2	G1	2 -
Overfilling	LS+A+	S 1	W1	-	-	-

Risk chart

according to DIN V 19250 and VDI/VDE 2180



* Normally technical industry safety measures

Advantages

- Transparency and plausibility of the decision-making process in an individual case
- Systematic investigation of the process and process conditions
- Individual solutions
- Risk-orientated fixing of safety measures
- Practice-orientated help
- Pre-existing and approved facts as a basis
- Legal certainty