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Toxic substances: ammonia, chlorine, inorganic acids, migration, sorbents, elimination of the environmental aftermaths

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DEVELOPMENT OF THE EFFICIENT TECHNOLOGY FOR ELIMINATING ENVIRONMENTAL AFTERMATHS IN TRANSPORT

Summary. We have carried out scientific research defining the ways of toxic loads migration, which polluted the environment as a result of transport accidents. We have defined the most important factors influencing the character of migration in the most widely spread soils of Ukraine and assessed the risk of toxicants penetration into the air, surface water sources or underground water carrying horizons. On the basis of the research we have worked out a number of proposals concerning organizational measures and technical decisions aimed at overcoming negative ecological consequences caused by these accidents. Wastes of some productions or accessible natural materials as well as up-to-date adsorbents and composites are considered to be the most suitable and perspective for the solution of these problems.

РАЗРАБОТКА ТЕХНОЛОГИЙ ДЛЯ ЛИКВИДАЦИИ ЭКОЛОГИЧЕСКИХ ПОСЛЕДСТВИЙ ТРАНСПОРТНЫХ АВАРИЙ

Аннотация. Нами были исследованы процессы миграции токсикантов в окружающей среде в результате транспортных аварий. Были определены наиболее важные факторы влияющие на миграцию токсикантов в грунтах, характерных для Украины, а также на испарение в атмосферу и фильтрацию в грунтовые воды. На базе этих исследований были разработаны организационные и технические подходы ликвидации экологических последствий транспортных аварий. Предложено использовать в качестве адсорбентов природные материалы, отходы некоторых производств.

Nowadays the feature of scientific and technological progress lies in growth of number of real and potential man-caused catastrophes.

Environment pollutions caused by accidents and acts of terrorism differ from many other man-caused disasters by that they have not gradual but sharp effect on an environment as a rule including prompt corresponding response. The most commonly used dangerous cargos transported by rail are oil products, dense inorganic acids, ammonia and chlorine.

However, there are many chemical agents which during emergency emission even in small volumes may cause severe damage to people, environment, facilities. It is typical that transportation of especially poisoning and explosive goods is carried out subject to implemented high level of preventive measures, special guard, etc. Whereas such toxic chemical compounds like chlorine, ammonia, inorganic acids etc., which one are mainly raw in many branches of industry, are emitted

also rather frequently into environment through transport accidents. According to information from Internet accidents including considerable emission of chlorine resulted in large human victims happened in Japan (1974), USA (1978, 1996), USSR (1987), Germany (1990), India (1994), Pakistan (1997). In addition, chlorine again found its poisoning application as a chemical weapon. So, during March - May 2006 (the latest act of terrorism took place on May 20) the Iraqi terrorists four times used explosive devices filled with chlorine.

In 2003, near Novosibirsk an emergency (damage of the tank car) spill of toxic mélange took place (mixture of sulfuric and nitric acids which is an oxidizer in a rocket bi-propellant). Large accidents entailed spills of acids are also known: near Tula in 2002, Perm in 2004, Vietnam in 2006, Polevskoi in 2006; Kiev-Chop highway in 2004, Novosibirsk – Baikal road in 2004.

Table 1 contains permissible and dangerous concentrations of some toxical gaseous goods [1].

Table 1

Physicochemical and toxic properties of some dangerous gaseous foods

Toxic agent	Density g/cm^3	Boiling point ^{o}C	Toxic properties			
			Injury concentration, mg/l	Exposure, min.	Lethal dose mg/l	Exposure, min.
Sulfurous anhydride	1,46	-10,0	0,4	50	1,4	50
Hydrogen fluoride	0,89	19,4	0,4	10	1,5	5
Ammonia	0,68	-33,4	0,2	360	7,0	30
Chlorine	1,56	-34,6	0,01	60	0,1	60

Technology of elimination of consequences of accidents with ecologically dangerous goods in the generalized aspect should consist of following blocks:

- isolation of evaporated clouds by generation of water curtain and their dissipation with the help of heat fluxes;
- neutralization of evaporated clouds: generation of fluid curtain with the help of neutralizing solutions, dissipation of clouds by an air - gas stream;
- isolation of spill of ecologically dangerous goods: banking of spill, collection of a liquid phase in pit - traps, spill covering by free-flowing sorbents, reduction of evaporation intensity by covering mirror of spills by a polymeric film, introduction of thickeners; treatment by neutralizing solutions or covering by neutralizing reagents;
- collection and next disposal of used sorbents and products of neutralization also;
- washing out the ground, next neutralization of sewage; cutting upper layer of the soil and its disposal.

At that, we proposed to use the following substance as neutralizing agents: for ammonia - ortophosphoric acid, solution of silicon phosphate or modified pyrogenic silica which contains acidic phosphate groups; for chlorine - sodium sulphite; for inorganic acids - lime slurries, soda solutions; for HF - lime milk, ammonia carbonate.

Structure of general process of accident and general layout of program on elimination of accident consequences is shown in Fig. 1.

Process flow of elimination of consequences of accidents with ammonia or its water solutions is shown in Fig. 2.

Ortophosphoric acid is supplied to the reactor - mixer in which water is supplied also for preparation of 50% solution. In case of large-scale accidents and necessity of consumption of significant amounts of neutralizing agent acid can be supplied directly from a railway tank-car intended for its transportation. Obtained solution is supplied into a pressure-tight head tank from which it is supplied to a zone of spill under pressure. After fulfillment of neutralization obtained solution is filtered from suspended particles and supplied to a reactor-neutralizer in which final

neutralization and components proportion bringing to value which is close to that one in marketable products are carried out. The rest of liquid ammonia from the damaged tank-car is delivered into the same reactor in case of no possibility to store it [2-3].

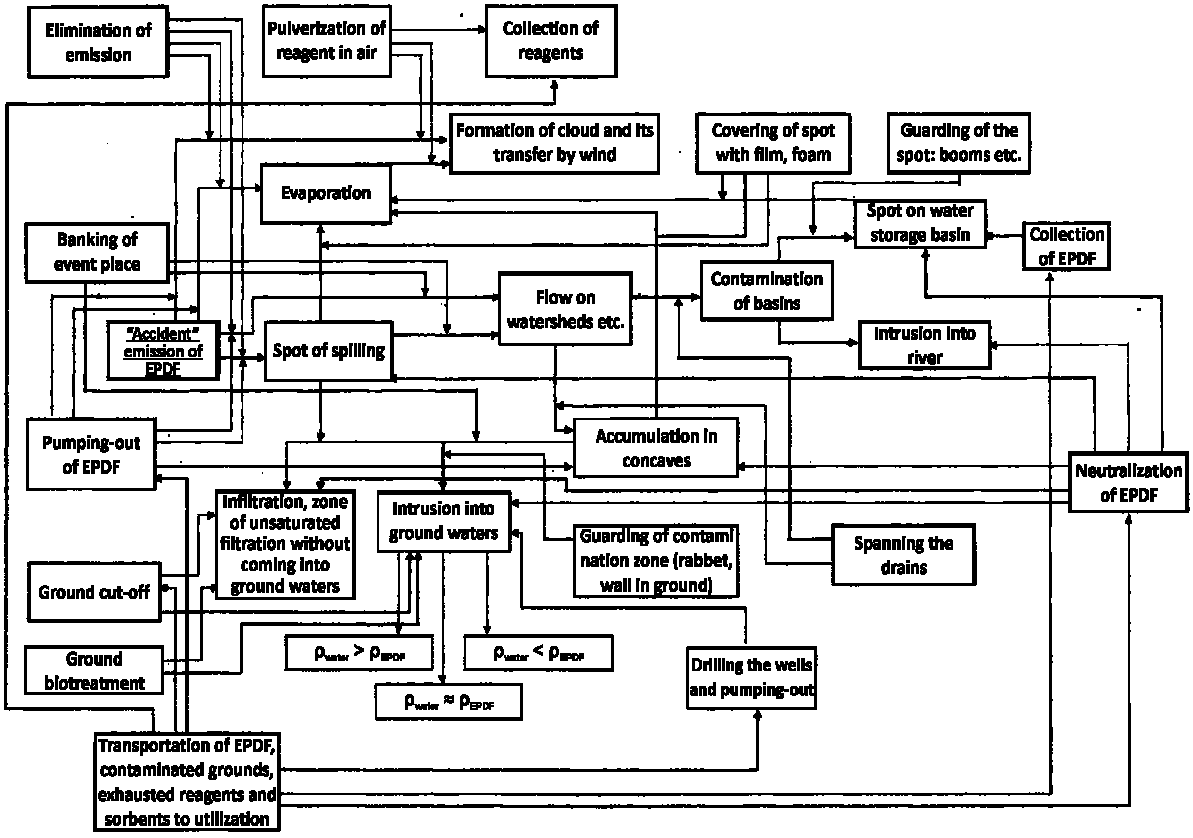

Fig. 1. Structure of general process of accident and general layout of program on elimination of accident consequences

Рис. 1. Структура общего процесса аварии и общей схемы программы ликвидации последствий аварий

Contaminated air above a zone of spill and also air from a damaged tank-car are supplied with the help of a fan into a scrubber spraying by solution of a phosphoric acid or silicon phosphate. Clean air is reverted into the atmosphere and liquid phase is delivered into reactor-neutralizer. All products of neutralization are combined in such way inside the reactor-neutralizer and are collected in tank-accumulators in the role of which a usual railway tank-car can be taken.

An important moment of neutralization process is not only selection of composition of efficient neutralizing agent, but its optimal amount also. In case of deficiency of an agent purpose of spill neutralization will be not reached, and at the same time excessive amount will result not only in unjustified expenditures but also would have negative consequences for an environment. In addition, significant excessive consumption of agents makes difficult process of elimination, raises the risk of pollution of reservoirs, can result in deficiency of equipment for pumping, storage and transportation of products, prolonged process of elimination, etc.

Process flowsheet which we used for disposal of ammonia spill can be utilized also for neutralization of spill of chlorine, HF and inorganic acids. Those types of absorbents are changed in pos.11 (Fig. 2) and absorber of a different construction is introduced. Applicable unification allows reducing cost of additional equipping of rescue trains and expanding nomenclature of ecologically dangerous goods to be neutralized.

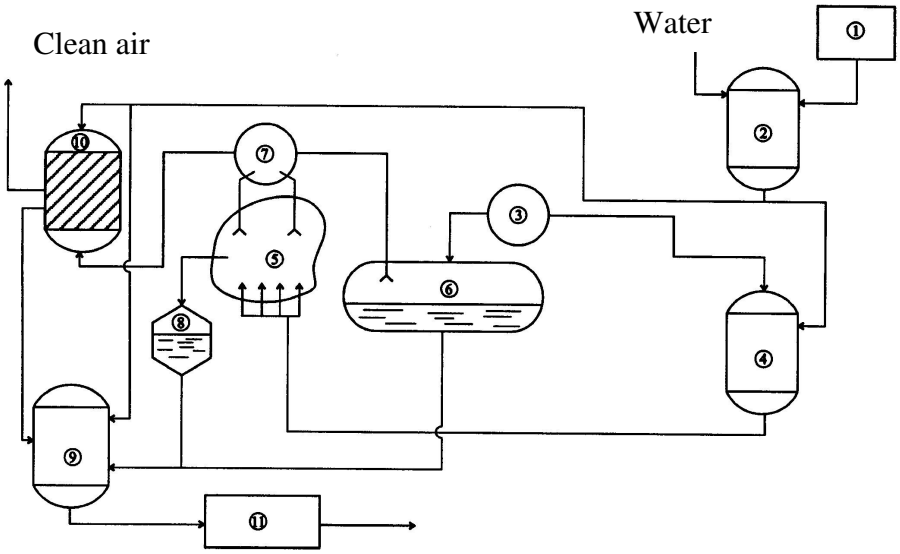

Fig. 2. Process flowsheet of elimination of consequences of accident with ammonia: 1 - tank for collection of neutralizing agent (ortophosphorous acid); 2 - reactor-mixer; 3 - compressor; 4 - head tank; 5 - zone of spill; 6 - damaged tank-car with residue of ammonia; 7 - fan; 9 - filter; 10 - reactor-neutralizer; 11 - scrubber; 12 - tank-accumulator for products of neutralization

Рис. 2. Принципиальная схема ликвидации последствий аварии с аммиаком: 1 - емкость для хранения нейтрализующего реагента (ортофосфорной кислоты); 2 - реактор-смеситель; 3 - компрессор; 4 - напорный резервуар; 5 - зона разлива; 6 - поврежденная цистерна с остатками аммиака; 7 - вентилятор; 9 - фильтр; 10 - реактор-нейтрализатор; 11 - скруббер; 12 - бак-накопитель продуктов нейтрализации

One of stages of elimination of consequences of accidents with ecologically dangerous goods lies in covering places of spill by absorbents or sorbents. Selection of absorbents is based on application of domestic, cheap and easy accessible natural materials or productions waste. E.g., in regions with advanced black metallurgy and production of building materials it is recommended to use dump slag and waste of foamed concrete; ash from heat power plants or boiler shops can be used in areas with developed heat and power generation industry. Sand, wood saw dust and chips, and other materials can be used also (sorbent types are given in Table 2) [4-8].

It was established that for successful solution of a problem of waste disposal the developed technology shall meet the following requirements [9-10]:

- ecological safety of introduced technology (no collateral, negative ecological phenomena);
- extent of waste cleaning from ecological toxicants shall meet requirements of state control, i.e. residual content of dangerous substances shall not exceed permissible concentration (MPC);
- economic efficiency of technology (profitability, low investments on capital construction and maintenance);
- minimal transport expenses (waste neutralization shall be carried out close to places of their formation);
- mobility of installation;
- small area required for installation disposition;
- universality of technology (possibility of the given technology application for different goods, treatment of liquid, paste-like and solid wastes);
- high rate of wastes neutralization;

Table 2

Characteristics of sorbents used in elimination of accidents

Adsorbent	Sorption capacity, kg/kg of adsorbent							Period of location on water surface	Caloric value with adsorbed product, KJ/kg	Cost of 1 kg spilled oil neutralization $
	Benzene	Toluene	H_2SO_4	HCl	HNO_3	NH_4OH	Oil and oil product			
ODM-F	0,75	0,75	1,45-1,5	0,85-0,95	1,2-1,3	1,1-1,2	–	0	4,0	0,32 (oil) 0,21 (acid)
Mordenite	0,92	0,92	0,96	0,96	0,96	0,96	–	0	4,0	0,67 (acid)
Silicagels	1,43-2,2	1,43-2,2	Disint.	Disint.	Disint.	1,42-2,21	–	0	4,0	0,33-0,52
Foamed vermiculite	4,0	4,0	-//-	-//-	-//-	0	–	0	4,0	0,25
Hydrophobic peat	1,5	1,5	-//-	-//-	-//-	0	–	120	17,0	0,12
Cellular graphite	20	20	57	56	56	40	–	80	35	0,13
Foamed isol	10	10				0	–	240	9	0,2
Activated carbon AR, DAU	1,67-1,82	1,67-1,82	1,65-1,8	1,8-2,1	1,8-2,1	0	2,0	5-6	35	0,25-0,33
Hydrophobic perlite	4,0	4,0	Disint.	Disint.	Disint.	0	10,0	48	4,0	0,15
Wood saw dust	1,0	1,0	-//-	-//-	-//-	0	6-8	0,5	5,0	0,03
Grained polyurethane foam	6	6	-//-	-//-	-//-	Disintegrated	10	240	8	0,2-0,43
Silica-alumina	2,2	2,3	-	-	-	0	–	0	4,0	0,33
Primesorb	8	7	Disint.	Disint.	Disint.	0	27	240	8	0,45
Synthetic	7	7	-//-	-//-	-//-	0	19,5	240	8	0,2
NewPig, США	4,5	4,5	-//-	-//-	-//-	0		150	8	0,2
Uremix-913			-//-	-//-	-//-	Disint.	28-53	250	–	–
STRG	–	–	–	–	–	–	55	–	–	–

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