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General description of the great Devnya's accident of a gas explosion

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ABSTRACT

The present study is devoted to the physical description and investigation of the causes and the dynamic evolution of the great Devnya's Accident 1986, (*VC*-gas cloud explosion on the territory of the Plant for Chlorine and *PVC* Production No. 2, happened on November 01, 1986 and destroyed fully the plant). The basic features of the destroyed thin-walled structures dynamically interacting with fillings of powder and liquids (silos, tanks, reactors, etc.) are shown. The basic lessons are accounted and described shortly.

1. BACKGROUND.

1.1. *Bulgaria, Varna, Devnya.* Varna is a district town on the north side of the Bulgarian Black Sea coast. Its importance as a sea port always has been exclusively high not for the nearby vicinity only, but even for whole Bulgaria occupying a very large area of the Balkan Peninsula. Its population is more than 300,000 people, and its basic living means is in the professions connected with the sea; partially with occupations in the tourism; partially - with the agriculture; great part of the people is occupied in the ship constructing industry and chemical industry. The latter is centered close to the small town Devnya disposed on 30 km from Varna in the so called "Chemical Valley".

In this valley, on the basis of the great local deposits of lime stone (i), the salt solutions ($NaCl_2$ plus H_2O) transported by a pipeline from the Provadia's salt stone mines (ii), the ethylene transported by a pipeline from the Burgas' oil Refineries (iii), and the new internal Varna West Sea Port (iv), starting from the second half of the 50-ies a system of 12 large chemical plants had been constructed. In this system until now are operating, e.g.: 1. Plant for Ammonia Production; 2. Plant for a Production of Artificial Fertilizers, (Nitric and Phosphor based); 3. Plant for Chlorine & *PVC* Production No. 2, (Dichloroethane, Chlorine, *PVC*); 4. Plant for a Soda Production No.2, (Caustic soda; Soda ash; Soda bicarb., etc.); 5. Plant for a Production of Carbide; 6. Plant for Cement Production; 7. Plant for Sugar Production: 8. Others...

1.2. *Characteristics of the VC-gas.* The vinyl chloride gas is heavier than the air and has sharp, not so pleasant and well recognizable smell. The vaporization temperature of the liquid *VC* at a normal atmosphere pressure of 1 *atm* is -10^0 C. The stoichiometric mixture with the air for the vinyl-based family of gases (vinyl-acetylene, divinyl, etc.) can be reached e.g. at concentration 90-100 g to 1 m^3 air. At normal temperature (higher than -10^0 C) the *VC* is a dangerous gas capable, in mixture with an usual air and initiated by a sparkle, to deflagrate causing devastating destructions of the corresponding engineering installations.

1.3. *Real conditions.* Time 6.55 AM; due to the early morning - bad visibility; wind with averaged velocity 2 m/s; size of the turbulence limited by the structures on open air of the workshop producing VC and dichloroethane; and temperature 0^0 C.

1.4. *Disposition of the workshops of the Plant for Chlorine and PVC Production No. 2 in Devnya.* The general disposition of the different plant workshops shows that the place of the workshop for *VC*-production is wrongly chosen, as the occasionally escaping gas following the wind direction can occupy the territory of all over the plant.

2. THE GREAT DEVNYA'S ACCIDENT.

2.1. *Description of the accident itself.* 01^{st} of November 1996, Saturday, 6.50 AM. Part of the workers of the different workshops of the Plant for Chlorine and *PVC* Production No. 2 started to prepare themselves for the change of the night shift, which had to be at 7.00 AM. Another part of the people, being on open air, had been troubled by a quite dense smell of *VC*-gas, coming from unidentified source. Some of them, immediately realized that the concentration of the escaped gas is exclusively dangerous and started to run in seeking a way to go out of the zone of *VC*-gas, and to call the other people in the workshops to safe them. At 6.55 AM a random sparkle probably from the electric installation initiated a giant explosion destroying the plant entirely... A full description of the accident one can find in Ref [1].

2.2. *The losses.* The losses were evaluated as 28.5 millions USD. 22 workers were killed. 10 people were wounded very hardly, 2 of them remaining entirely blind for ever. The losses due to the stopping of the production process for two years (i), and the losses due to the losing of the positions on the European chemical market (ii) were not taken into account.

3. DESTROYING FACTORS.

3.1. *Destroying factors.* The Great Devnya's Accident appeared to be a typical accident due to a deflagrating explosion. The most probable evolution of the accident was proved by the investigations of its possible variants. It shows that the most dangerous accidental loads are realized by: (i) fires and high temperatures; (ii) pressure of the air shock waves (ASW); (iii) missiles and flying fragments; and (iv) local seismic waves.

3.2. *Two pictures of the Polymerization Workshop.* On Fig.1 the picture of the Polymerization workshop before the accident is shown. By numbers 1 and 2 both pairs of reactors are denoted. By number 3 the pair of two degasators is denoted. Outside, but behind is seen a tall cylindrical tank. Three concrete plates form two working levels and a roof, but all the technologic equipment is on open air. On Fig.2 the four non-broken reactors and both degasators before the full dismantling after the accident are shown. All destroyed structures are avoided.

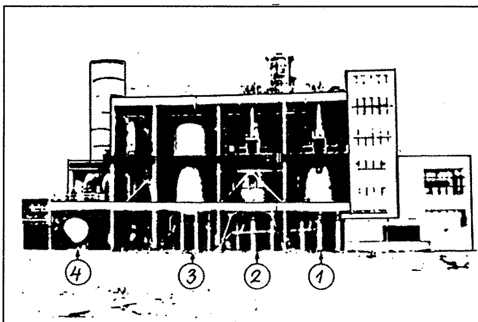


Fig. 1.

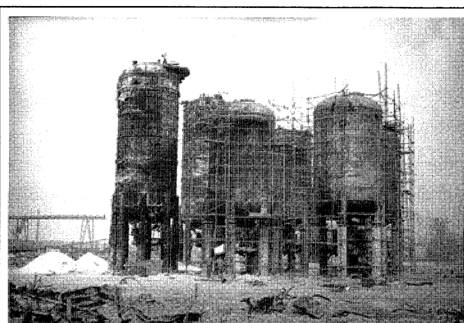


Fig. 2.

4. RESPONSE OF FILLED THINWALLED SILOS

4.1. *The places of the silos in the technological scheme.* The silos served as temporary stores for the *PVC* powder in two places of the technological scheme: (i) the drying workshop, in which three "small" silos were disposed; (ii) the terminal high scaffold bridge on which 8 silos had been mounted. Two of them were of "small" volume (150 m^3), and six were of "large" volume (780 m^3). These silos served as a temporary stores for the ready production (*PVC* powder) before its recharging in the special railway transport hoppers.

4.2. *Structural components.* Below on Fig.1 the dimensions of the silos of both types are shown. The basic structural components of the silos are:

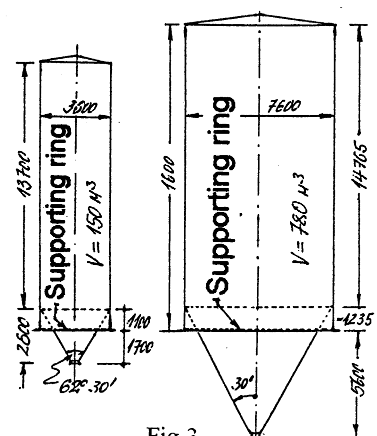


Fig.3.

(1). The long cylindrical shell serving as a basic body for the product stored (PVC powder).

(2). The short supporting cylindrical shell (called "supporting ring").

(3). The conical-shell hopper serving as a bottom holding the contents.

(4). Conical roof shell.

All these components are well observed on Fig.3, and so they do not need additional explanations.

4.3. *Typical destructions.* The shells of the silos are destroyed by exclusively strong vacuuming realized by a specific consequence of the loading action of the explosion pressure.

As a typical sample Fig.4 shows such destruction.

4.3.1. *An upward explosion pressure.*

Results: □ the shell of the conical bottom hopper is deformed upward braking (fully or partially) the welding link between the wall of the silo shell and the edge of the hopper shell □ the PVC powder is pressurized as a bottle cork; □ the short cylindrical shell of the supporting ring is blown out obtaining typical deformation.

4.3.2. *Under the action of its own weight* and (probably) of the high outside pressure this cork together with silo shell starts to go down and breaks (finally - fully) the bottom hopper welding.

Results: □ the over-pressed powder starts to escape with high velocity; □ vacuum effect and large nonlinear deformations of the silo shells occur.

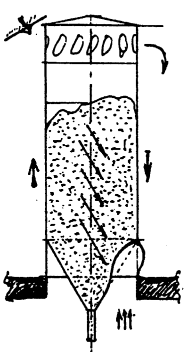


Fig.4.

4.3.3. *The supporting rings* probably are destroyed under the action of the upward directed pressure which blows out them creating the corresponding eccentricity followed by the consequent impact application of the weight (the whole silos), seen on Fig.4. Really the data and their correct interpreting show that under the action of the upward acting pressure the whole silo together with the contents has jumped upward.

4.3.4. *The conical hopper shells* of the large silos had been torn off from the cylindrical shell and fell down from the scaffold bridge. over the railway transport hoppers The conical hopper shells of the small silos Fig.5 were found to be joined to the supporting cylindrical shells, but all the 5 of them had characteristic longitudinal ribs, well seen on Fig. 5. Their probable origin is under discussion. One of the small silos was remained on its place on the scaffold bridge. This helped us very essentially, permitting to check the presupposed working hypotheses on place.

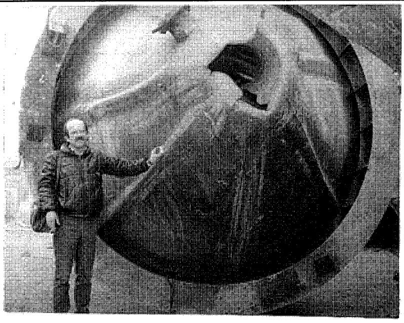


Fig.5.

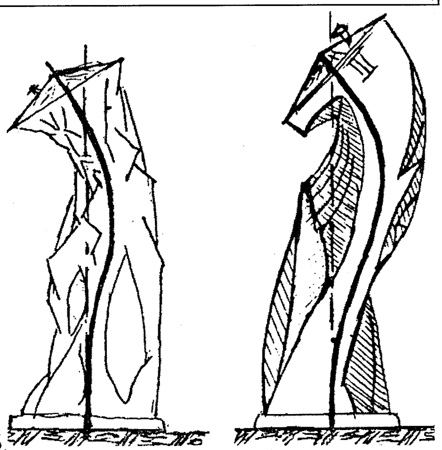


Fig.6.

4.3.5. *General considerations.* On Fig. 6 the character sketches of two of the destroyed large silos are given. On Fig.7 a photo-picture of a typical destroyed large silo is shown. On Fig.8 and Fig.9 upward views of two different large silos (lying on the ground) are shown. They prove that 5 large well expressed semi-waves in circumferential direction were formed as a result of the cylindrical shell destruction. This fact can be used for considerations on the inverse problem.

In taking e.g. the forced circular frequency $\sigma_{1,5}$ as responsible for the deformation observed, one can find the velocity of the escaping corky powder PVC. On Fig.10 a specific deformation of a small silo from the Drying Workshop is shown. Its comments can be found in the text after Fig.16.

5. RESPONSE OF THE PARTIALLY FILLED THINWALLED TANKS

5.1. *The places of the tanks in the technological scheme of Devnya's Plant for Chlorine and PVC production No.2.* The destroyed thin-walled vessels partially or fully filled with liquids had been used on different

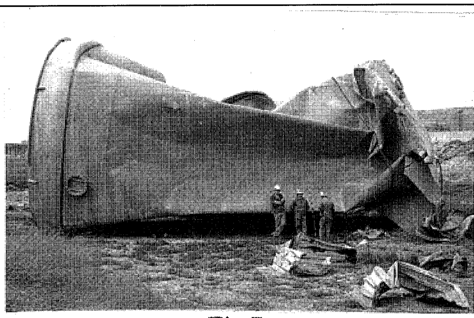


Fig.7.

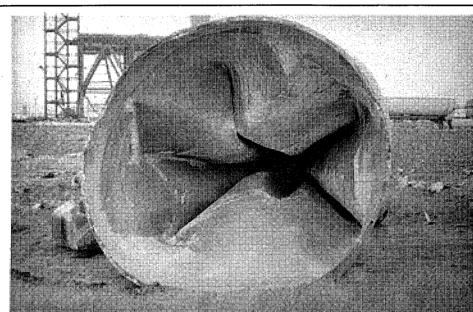


Fig.8.

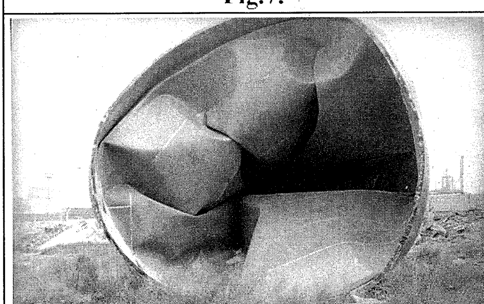


Fig.9.

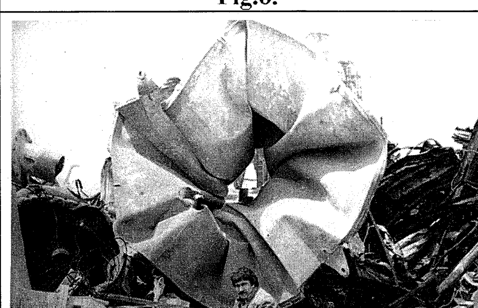


Fig.10.

places of the technological scheme of the *PVC*-plant. Below some of these vessels and tanks are accounted: □ horizontal cylindrical tanks for *VC* processing; □ vertical cylindrical tanks for dichloroethane storage; □ vertical cylindrical vessels used for the reactors; □ vertical cylindrical vessels used to avoid the dissolved gas and the gas bubbles (degasators); □ vertical cylindrical vessels used to average the fracture needed of the PVC powder; □ large horizontal cylindrical tanks used for a storage of a liquid VC; □ spherical tanks used for a storage of a liquid *VC*; □ horizontal cylindrical tanks of a storage of liquid chlorine; □ horizontal cylindrical tank for a storage of sulfuric acid; □ others, non-identified here places of vessels use.

All these vessels are exclusively important for the correct operation cf the technological scheme under consideration, but they are generally useful in reactor technology.

5.2. *Structural components.* 5.2.1. *The basic component of the vertical cylindrical tanks* is the short (or middle length) metallic thin-walled circular cylindrical shell. Weld joint links this shell with the steel sheet bottom lying on especially prepared bed. Another weld joint links the shell with a tin-walled conical roof shell. The destroyed vertical cylindrical tanks in the case are of the category of the small tanks.

5.2.2. *The basic component of the horizontal tanks* is the short, middle (or long length) metallic circular cylindrical shell. Two weld joints link both edges of this shell with two circular walls closing the shell and turning it into one-bounded spatial domain (cavity) able to hold liquids. These walls are shaped as circular planes, or as oblate-ellipsoidal (or shallow spherical) shells. Depending on their lengths, the tanks are mounted on two or more concrete supports.

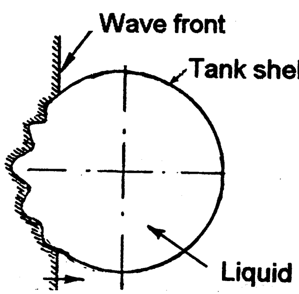


Fig.11.

5.3. *Analytical sample cases.* For the future investigator it is important to know the sample cases of the possible destructions solved analytically. So, one will be able to estimate the corresponding loading. Obviously this can be useful component of the inverse problem formulations and solutions.

5.3.1. *Transversal irradiation of a cylindrical shell,* [02]. It is known that in case of a real irradiation of a circular cylindrical shell filled with liquid by a simple shock wave the frontal part of the cylindrical surface of the shell deforms itself in several characteristic waves, as it is shown on Fig.11. The depths of the shell wave profiles depend on the velocity of the falling wave field, on the density of the outside fluid serving as a media of the falling SW, and the characteristics of the inside fluid (liquid), see *Mnev & Pertzev* [02].

5.3.2. *Longitudinally irradiated cylindrical shell. Ishlinskii & Lavrentiev* [03] analytically and experimentally had proved that the transversal sections of an empty thin-walled long circular cylindrical shell, after a longitudinal irradiation by an air shock wave deform themselves in developing e.g consequently 6, 5, 4, 3, and 2 well expressed and deep waves along the circular coordinate of the shell, as it is shown on Fig.12.

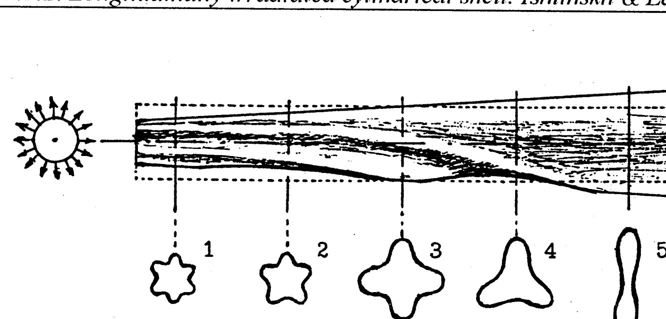


Fig.12.

5.4. *Three cases of real destruction.* 5.4.1. *The vertical cylindrical tanks* storing liquid dichloroethane are destroyed just following the scheme of the first theoretical pattern. However, the sample sketch is shown on Fig.13, a confirming photo-picture being given on Fig.14.

5.4.2. *A horizontal tank.* A sketch of a destroyed "small" horizontal tank for hot liquid *VC* processing is shown on Fig.15. The temperature of the liquid *VC* in this tank had 96^0 C, which after break, at 0^0 C and normal atmosphere pressure explosive-like turned itself into gas and together with the air formed the explosive mixture causing the accident under consideration.

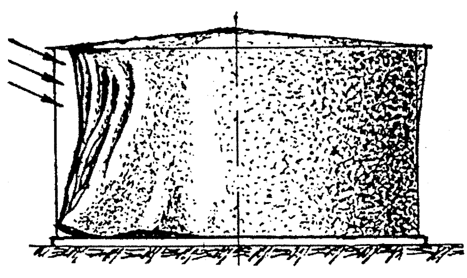


Fig.13.

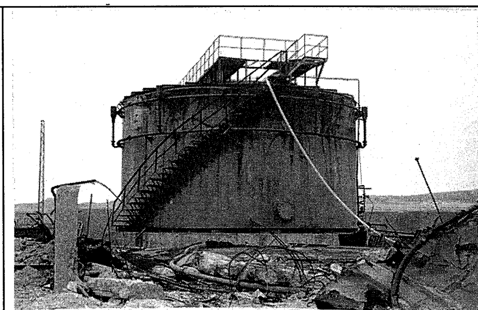
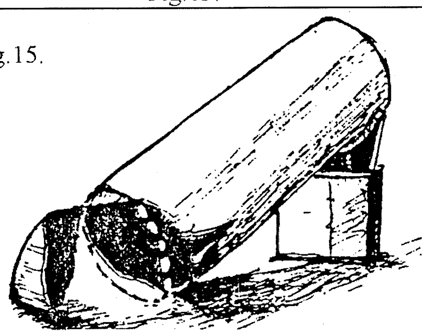


Fig.14.

Fig.15.



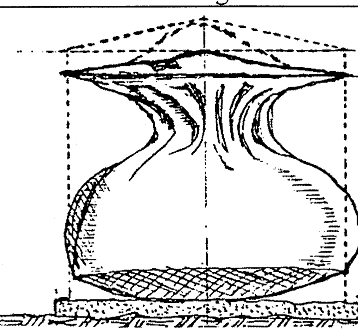


Fig.16.

5.4.3. *An exotic tank deformation.* An exotic peristaltic destruction (large deformation) of a vertical cylindrical tank *partially filled with liquid (dense oil)* is shown on Fig.16. Analogous was the deformation of one of the "small" silos shown on Fig.10. Both cases demonstrate that the random combination of the causes produce particular action of the pressure, and the corresponding particular deformation of the thin-walled structures, if there are cavity zones in the filling. In both cases the great rigidity of the roof conic shells is well observed.

Fig.17.

6. RESPONSE OF THE REACTORS

6.1. The places of the reactors in the technological scheme. The four *PVC* reactors have been designed by KHD-PRICHARD GMBH, KÖLN. Preliminary we would like to say, that independently of the fact that the epicenter of the explosion was quite close to the reactor battery, and independently that the concrete structures, pipes, pumps, etc. had been destroyed, the precise geometric and metallographic X-ray investigations did show that the reactors as geometric structures, as well as a metallic material, were not destroyed at all. This is seen by the view on Fig.17 and Fig.2. However the Polymerization Workshop was disposed close to the silos scaffold bridge and in contrast all of the silos were fully destroyed, Ref. [01].

6.2. *The enigma of the anchor studs*. Every one of the reactors has been supported by six tubular column legs. Everyone of the columns has been anchored by four powerful studs. Many of these studs were pulled out on 12-18 mm and bent in different directions, Fig.18. A special investigation did show that the shear stresses due to the adhesion between the stud surfaces and the concrete were destroyed (absent). The only logic explanation is that micro-seismic motion of the soil downward is the cause. Independently of this explanation the Author thinks, even until now, that something enigmatic has place in these strange stud deformations. Details on this matter can be found in Ref. [01], (pp. 67-72), and in Ref. [02], (pp. 199-200.).

7. GENERAL LESSONS OF THE ACCIDENT

7.1. *On the disposition of the workshops in the time of the preliminary design*. It is exclusively important for the design engineers, that so called *"Wind Rose"* providing the *probabilistic distribution of the directions and the intensities* of the winds on the plant site has to be taken into account in determining the disposition of the workshops in arbitrary plant (depending on the corresponding technology). If a wind of given *Kolmogorov's* size turbulence
can serve as an agent translating dangerous gases produced in any of the workshops, it is important *these workshops to be put on the end of the plant court following the wind direction.* Moreover, after the last dangerous workshop is to have enough free distance for the natural dissipation of the dangerous quality of the corresponding gas: Ref. [01], (pp. 96-104), and Ref. [06], (pp. 206-214).

7.2. *On the jet shooting length of the escaping liquids*. For the vessels under high pressure it is important to known the probable distance of the direct jet shooting length of the dangerous liquid in case of accidental breaks and flaw appear in the vessels walls: Ref. [01], (pp.112-119) and Ref. [06], (pp. 244-252); see also Ref. [07].

7.3. *On the voice material of the witnesses*. The official "voice material" (original audio-records of the witnesses evidences) is exclusively important. But the official investigators connected with the Juridical Power have to verify this material with the physical estimation of the Engineering Investigators. The matter is in the natural stress state of the witnesses after the shock of the accident and the psychological spiritual disposition caused by the miracle that the witness is alive but the friend of him is dead... We discovered many examples of wrong evidences, caused by the natural desire of the survived workers to show e.g any heroism: Ref. [01], (pp. 120-128), and Ref. [06], (pp. 220-239).

7.4. *On the investigation method*. Of course, in time of an investigation of an accident of such level some specific methodical techniques have to be used. Here related with the need to solve many times the inverse problem at fussy information, as basic readings on deterministically solved problems we would like to recommend the books on non-stationary fluid-structure interaction of *Grigolyuk & Gorshkov* [04] and *Guz & Kubenko* [05].

7.5. *Safety lessons*. In the last chapter of Ref. [01] the lessons of the catastrophe are described. In few words they can be formulated with the sentences:

7.5.1. *The technological culture and the technological discipline* of the people designing, or working with dangerous technologies have to be elevated to the level of the highest possible professionalism.

7.5.2. Independently of the previous point, *the different safety inspections of the follower alert systems* (fire, electricity, water, computing control, etc.) have to be realized in order and frequency to ensure the requests of the previous point in *permanently unsleeping conditions.*
7.5.3. *The basic cases of the earlier accidents* in the world have to be known to all the working staff of the plant. And the most important - the people from the follower and monitoring system has to know what is the technological system which can prevent the accident, if dangerous conditions are created. In the same time the workers and operators have to know the basics of their life safety...
7.5.4. *The dead zones* around everyone dangerous unit have to be well known to the operators and workers and the *evacuation ways and means* to be known and visible independently of the alert conditions of different types.

ACKNOWLEDGEMENTS.

Here we would like to mention the constructive role of Mr. N. I. PASKOV, M.E., who was charged by the duty to help us in the accomplishment of the real technical investigations on the plant place in 1987. All the photo-pictures are made by Mr. P. KALOYANOV. Besides their essential technical help, we would like to mention the financial help of the Director Mr. K. TSONEV, Ch.E., and of the support of the directors of the Higher Board governing the whole Chemical Complex Mr. STOYAN ILIEV, M.E., Mr. N. SLAVOV, and the CE Director Mr. STOYAN EVTIMOV. In our labor a part of their powerful influence, so needed in those days, can be realized as exclusively helpful.

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ADDENDUM.

In several lectures (see Ref. [08]) on different seminars and conferences parts of the expert investigation were represented, but they have not been published until now. The material gathered here could not describe all the divers aspects of the investigation.