Scuola Politecnica

La sicurezza in ambito industriale ed ambientale

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LA SICUREZZA NELL'INDUSTRIA DI PROCESSO: LEZIONI DAGLI INCIDENTI

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STATISTICHE SUGLI INCIDENTI INDUSTRIALI

Deaths	Incident
3,787 to 19,000+	Bhopal disaster (India, 1984)
1,549	Benxihu Colliery explosion, China, 1942
1,129	Collapse of the Rana Plaza (Savar Upazila, Dhaka District, Bangladesh, 24 April 2013)[18]
1,099	Courrières mine disaster, Courrières, France, 10 March 1906
687	Mitsubishi Hōjō, Kyūshū, Japan, 15 December 1914
682	Laobaidong colliery coal dust explosion Datong, China, 9 May 1960
568+	Texas City Disaster (Texas City, Texas, United States, 16 & 17 April 1947)
512	Sumitomo Besshi bronze mine area, landslide with debris flow disaster, Niihama, Shikoku, Japan, 1899
500+	San Juanico Disaster (Mexico City, 19 November 1984)[19]
458	Mitsui Miike Coal Mine disaster Mitsui Miike, Ōmuta, Fukuoka, Japan, 9 November 1963[20]
…	….

(fonte: en.wikipedia.org)

STATISTICHE SUGLI INCIDENTI INDUSTRIALI

L'elenco riporta solo I primi 10 incidenti della tabella originale.

A questi, che vanno sotto l'indicazione di "incidenti rilevanti", vanno aggiunti i vari incidenti che sono avvenuti anche in industrie o aziende più piccole e che hanno causato un minor numero di morti ma che avvengono sempre per mancata osservanza delle più basilari norme di sicurezza.

Un esempio di ciò è dato dalle morti per asfissia o intossicazione per l'accesso in ambienti confinati (cisterne, serbatoi, …) che puntulamente si sono verificati anche in Italia.

INCIDENTI INDUSTRIALI: FONTI DI INFORMAZIONE ONLINE

Ampia rassegna di incidenti industriali disponibile online:

www.wikipedia.org

www.csb.gov (U.S. Chemical Safety Board)

emars.jrc.ec.europa.eu (EU Major Accident Reporting System)

www.factsonline.nl

www.epsc.org (European Process Safety Centre)

….

INCIDENTI

Argomento di questa presentazione:

1974 – Flixborough (esplosione)

1984 – Bophal (nube tossica)

1984 – San Juan – Città del Messico (esplosione, effetto domino)

Si tratta di tre eventi che, assieme a molti altri (ad es. quello di Seveso del 1976 e quello della piattaforma Deepwater Horizon del 2010 nel Golfo del Messico) hanno avuto un grande impatto nell'opinione pubblica e hanno imposto ai Governi di rivedere o di implementare la legislazione sulla sicurezza.

1974 - L'INCIDENTE DI FLIXBOROUGH (UK)

E' la più grande esplosione in tempo di pace avvenuta in UK

Data: sabato 1 giugno 1974

Località: impianto Nypro a Flixborough

Morti 28 operai e 26 feriti gravi

Danni rilevanti estesi nel raggio di 8 km dall'impianto

STODIA DELL'IMPIANTO

Impianto di produzione di caprolattame (un precursore del nylon) costruito dalla DSM nel 1967

Processo adottato: idrogenazione del fenolo:

$$C_6H_5OH + 2H_2 \rightarrow (CH_2)_5CO$$

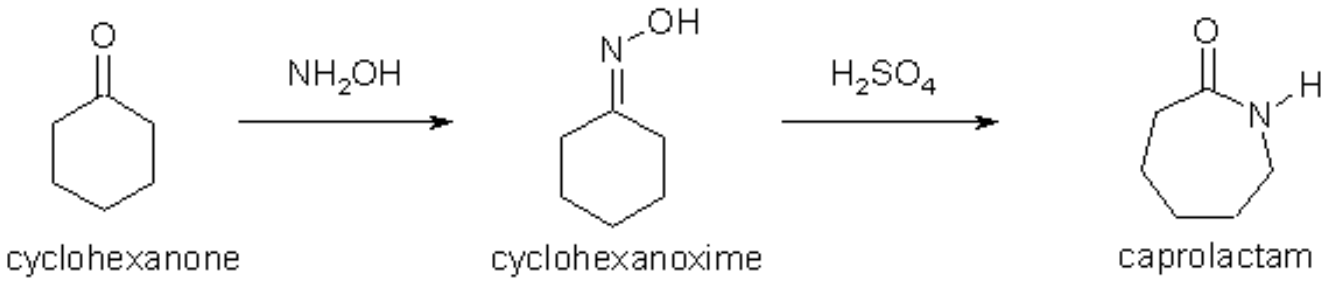
1972: nuovo processo basato sull'ossidazione del cicloesano, produzione 70000 tonn/anno

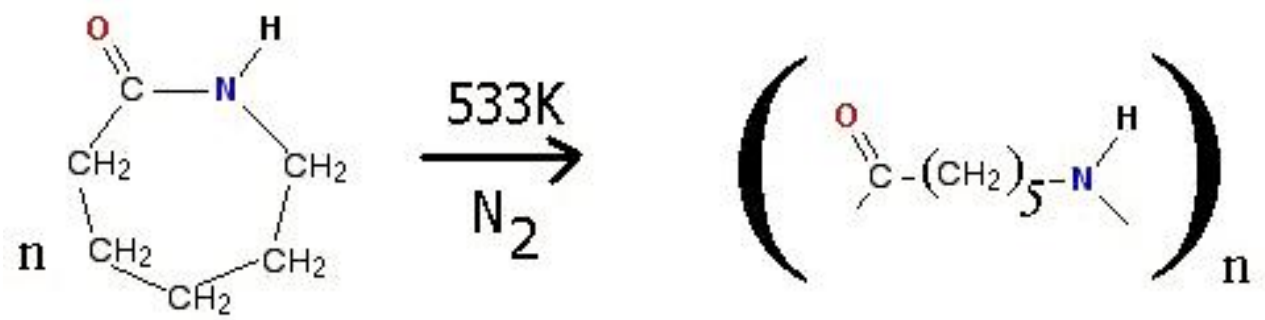
Nuovo processo molto più pericoloso del precedente

IL VECCHIO PROCESSO

$$C_6H_5OH + 2H_2 \rightarrow (CH_2)_5CO$$

Cyclohexane **Cyclohexanone**

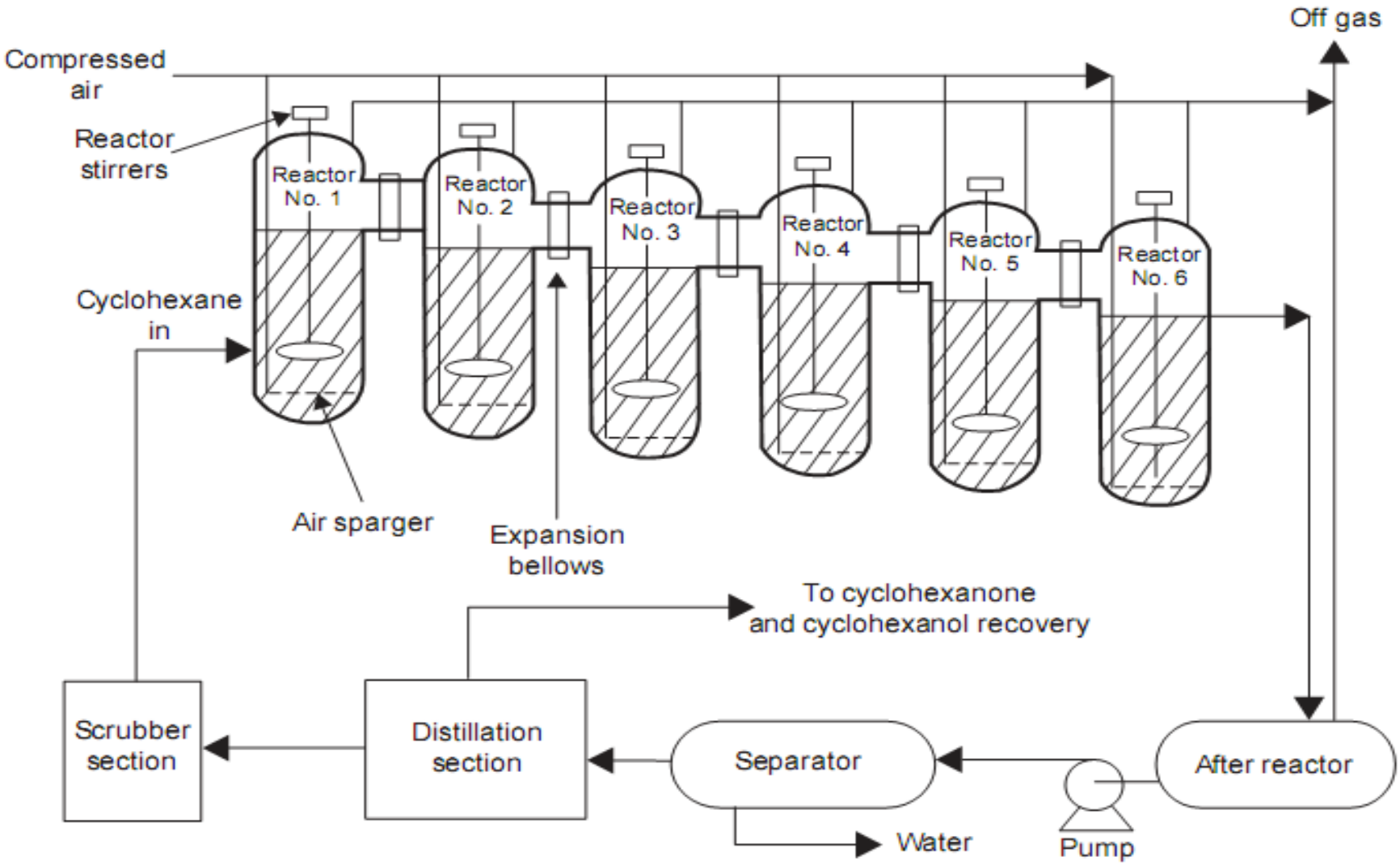




Caprolactum **Nylon6**

1974 - L'incidente di Flixborough (UK)

SIMPLIFIED FLOW DIAGRAM OF CYCLOHEXANE OXIDATION PLANT BEFORE MARCH 1974 (WHITTINGHAM, 2005)



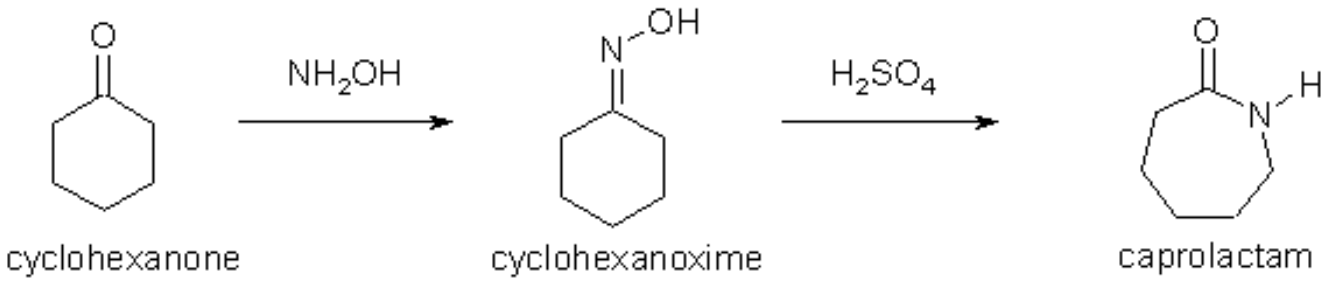
1974 - L'incidente di Flixborough (UK)

IL NUOVO PROCESSO

1) $C_6H_{12} + O_2 \rightarrow (CH_2)_5CO + H_2O$

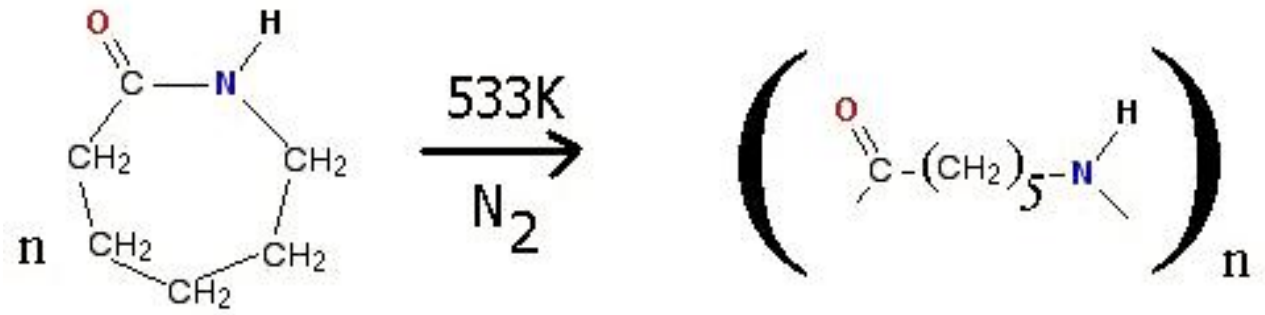
Cyclohexane **Cyclohexanone**

2)



cyclohexanone cyclohexanoxime caprolactam

3)



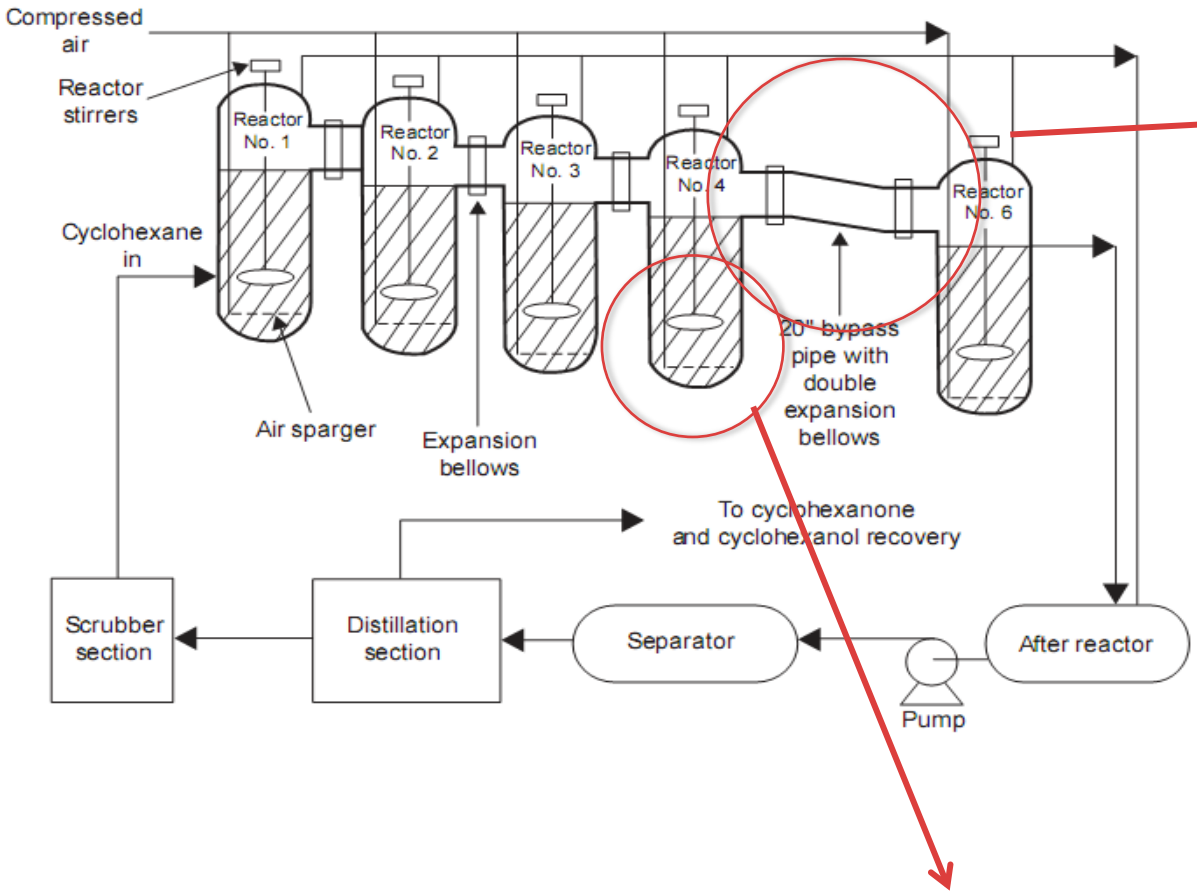
Caprolactum **Nylon6**

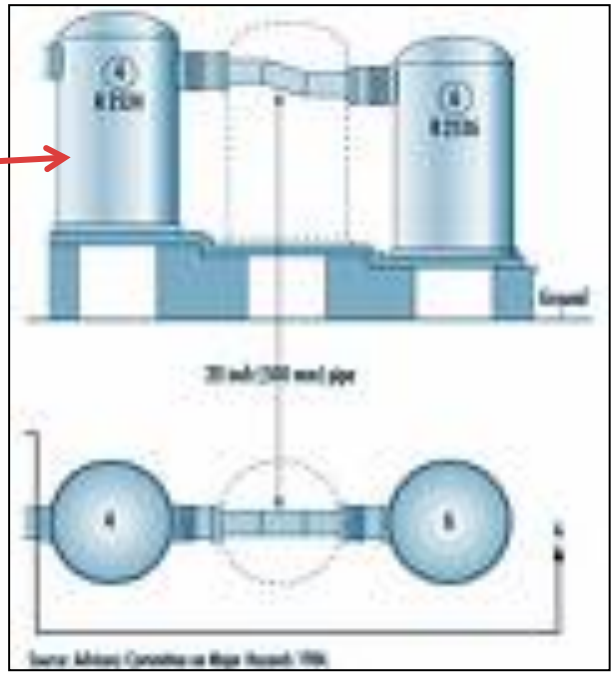
1974 - L'incidente di Flixborough (UK)

SEQUENZA DEGLI EVENTI: ANTEFATTO

1. A causa di una perdita al reattore 5 va fuori uso.
2. Per non fermare la produzione si decide di bypassarlo, realizzando un collegamento temporaneo tra i reattori 4 e 6.
3. Le connessioni originali erano fatte con tubazioni da da 28”, l’installazione del bypass viene fatta con un tubo da 20” (mancavano quelli da 28”…) ed eseguita da personale non specializzato
4. Nessun ingegnere meccanico ha supervisionato il lavoro
5. Viene effettuato un test di tenuta con aria compressa, ma nessuna prova idraulica di resistenza alla pressione sulla nuova connessione.

SIMPLIFIED FLOW DIAGRAM OF CYCLOHEXANE OXIDATION PLANT AFTER MARCH 1974 (WHITTINGHAM, 2005)





Agitatore guasto

1974 - L'incidente di Flixborough (UK)

SEQUENZA DEGLI EVENTI: IL RIAVVIO

6. L'impianto viene rimesso in funzione, operando normalmente fino venerdì 31 maggio, quando viene fermato per piccole riparazioni
7. Mattina del1 giugno: si eseguono le operazioni per il riavvio. Si ricarica l'impianto con cicloesano liquido e si avvia il riscaldamento della carica sino alla temperatura di reazione.
8. Il sistemaa viene inizialmente pressurizzato a 4 bar con azoto, dopodichè la pressione aumenta a causa dell'evaporazione del cicloesano. la condizione finale da raggiungere è di 9 bar e 150°C.

SEQUENZA DEGLI EVENTI: IL RIAVVIO

9. La procedura di starup viene monitorata: si osserva un innalzamento anomalo della pressione nel reattore n. 1 che raggiunge la pressione di 8.5 bar nonostante la temperatura sia solo di 110 °C.

10. La discrepanza nel reattore n. 1 indicherebbe la presenza di acqua ma non viene considerata.

11. La procedutra di avvio prosegue finchè, alle 16:50, un addetto del laboratorio vicino al reattore avverte il rumore di una fuga di gas e l'odore tipico associato ad una nucola di idrocarburi.

SEQUENZA DEGLI EVENTI: L'INCIDENTE

9. Ore 16:53 del 1 giugno 1974: si verifica una massiccia esplosione con una potenza stimata (a posteriori) equivalente a 15-45 tonnellate di TNT.
10. Il rumore dell'esplosione viene percepito a più di 40 km dall'impianto e causa danni catastrofici nel raggio di 8 km.
11. 28 operai restano uccisi: 18 nella sala controllo, 9 nel resto dell'impianto e un autotrasportatore colpito da infarto. I morti sarebbero stati centinaia se l'incidente non fosse avvenuto il sabato.
12. nelle successive indagini la tubazione di 20" viene ritrovata danneggiata, ma non dall'esplosione!

ANALISI POST-INCIDENTALE

- Le conclusioni degli esperti sulle cause dell'incidente attribuiscono alla rottura del bypass da 20" la responsabilità principale della fuga di gas e della successiva esplosione.

- Vengono formulate due ipotesi sulla rottura, basate sul non adeguato dimensionamento del bypas, ma nessuna di esse è completamente soddifacente. (il bypass ha funzionato correttamente per due mesi, prima di collassare …).

ANALISI POST-INCIDENTALE: IPOTESI ALTERNATIVE

L'incidente di Flixborough ha attirato l'attenzione di molti esperti che hanno considerato ipotesi alternative alle conclusioni dell'inchiesta ufficiale

La più accreditata spiega l'incidente con la presenza di acqua nel reattore 4, associata al fatto che il miscelatore dello stesso fosse fuori uso.

Cicloesano e acqua sono scarsamente miscibili, formano però un azeotropo che bolle a temperatura minore rispetto alle due sostanze. Ciò implica che la pressione nel reattore possa essere aumentata molto più di quanto atteso e causare la rottura del bypass (altrimenti inspiegabile alle pressioni di esercizio)

CONCLUSIONI:

- Analisi degli errori umani: La tabella successiva indica diversi tipi di errore.
- Causa diretta: la rottura del bypass da 20 inch ha provocato il rilascio della nube di cicloesano che, innescata, è esplosa (UVCE).
- Causa originale: si è scelto di utilizzare un bypass (malprogettato) piuttosto che eseguire una indagine sul motivo della rottura del reattore 5.
- Incerti I motivi della rottura del bypass.

Human error analysis of the Flixborough disaster **(Whittingham, 2005)**

Cause	Description	Type of error or other failure	Systemic cause or preventive action
Direct cause	Failure of the 20 inch bypass pipe causing a massive release of cyclohexane vapour to the atmosphere	Operator error (implied)	Since the inquiry was unable to establish a definitive cause (only the one with the highest probability), then by implication, the direct cause had to be over-pressurization of the system by the operators at start-up.
Root cause	The cause of the 20 inch bypass failure was either:		
	Over-pressurization during start-up or,	Management error	Inadequate design and support of the bypass pipe in a dog-leg configuration due to lack of mechanical engineering expertise.
	Mechanical displacement of the bypass pipe by slugs of liquid carried forward from reactor No. 4	Design error	A failure on the part of the designers to recognize or communicate the consequences of not operating the reactor stirrers at start-up.
Contributory causes	Failure by local management to understand the hazards of the cyclohexane process	Management error	This knowledge might have prevented the expedient construction of the 20 inch bypass pipe, due to the perceived hazards of a large unconfined vapour release.
	No qualified mechanical engineer on-site	Management error	Changes to a design should be overseen and authorized by properly qualified personnel.

CONSIDERAZIONI SULLA SICUREZZA ("LESSONS FROM DISASTER")

- Maggiore conoscenza del processo e dell'impianto.
- Ridurre le quantità di sostanze pericolose trattate (*ciò che non c'è non può essere rilasciato nell'ambiente*)
- Effettuare analisi di sicurezza (tipo HAZOP)
- Usare gli stessi standard dell'originale quando si effettuano modifiche all'impianto
- Costruire sale controllo e edifici bunkerizzati attigui alle aree a rischio, in grado di resistere ad eventuali esplosioni.

A seguito di questo incidente le autorità anglosassoni hanno incrementato le richieste di sicurezza per impianti analoghi, implementando la legislazione in materi di rischio industriale.

1974 - L'incidente di Flixborough (UK)

1984 – BOPHAL ...

A pesticide plant in India produced the compound Methyl Iso-Cyanate (MIC) as an intermediate product in the process.

MIC is an extremely toxic and unstable substance and even in very small quantities is fatal.

Large quantities of the MIC were stored in steel tank. The tank had many safety features to maintain the product in a safe and stable form.

Economic pressures meant that most of these features were abandoned to save money.

.... 1984 – BOPHAL

Water, inadvertently entered the storage tank and caused an exothermic, runaway reaction to occur.

The MIC boiled up and MIC vapour was expelled through the bursting disc vent.

The scrubber and flare stack **were in-operational** so the MIC vapour was discharged directly to atmosphere.

The wind carried it as a plume over the adjacent city of Bhopal where the victims were living.

DAMAGES

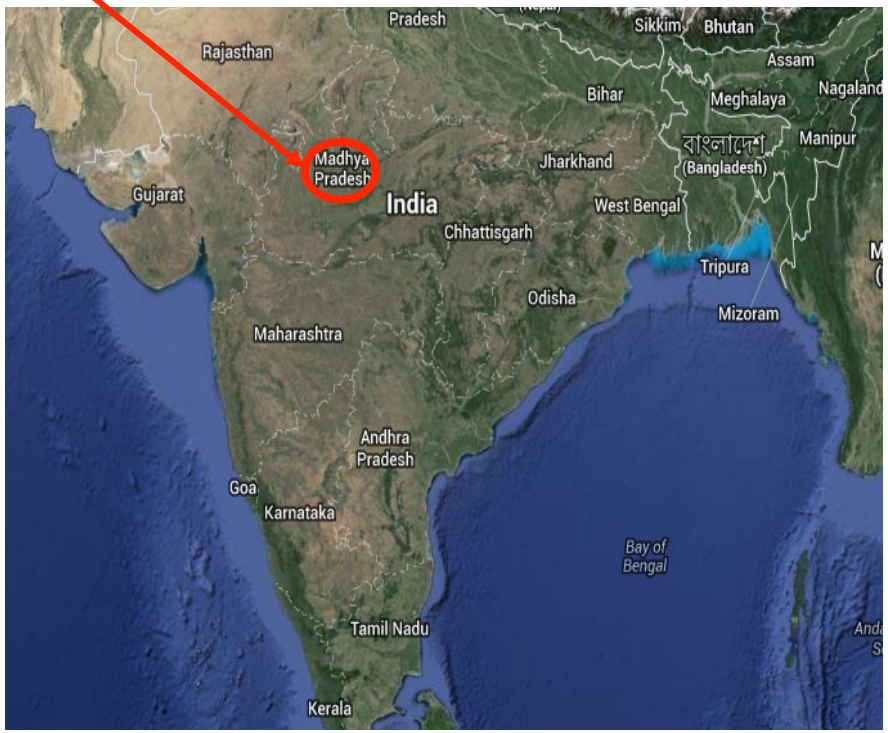
- 2000 DIED IMMEDIATELY (IT IS BELIEVED THAT MORE THAN 15000 PEOPLE DIED AS A CONSEQUENCE OF CHEMICAL EXPOSITION AFTER THE INCIDENT)
- 300000 WERE INJURED
- 7000 ANIMALS WERE INJURED, OF WHICH ABOUT ONE THOUSAND WERE KILLED.

1984 - Bophal

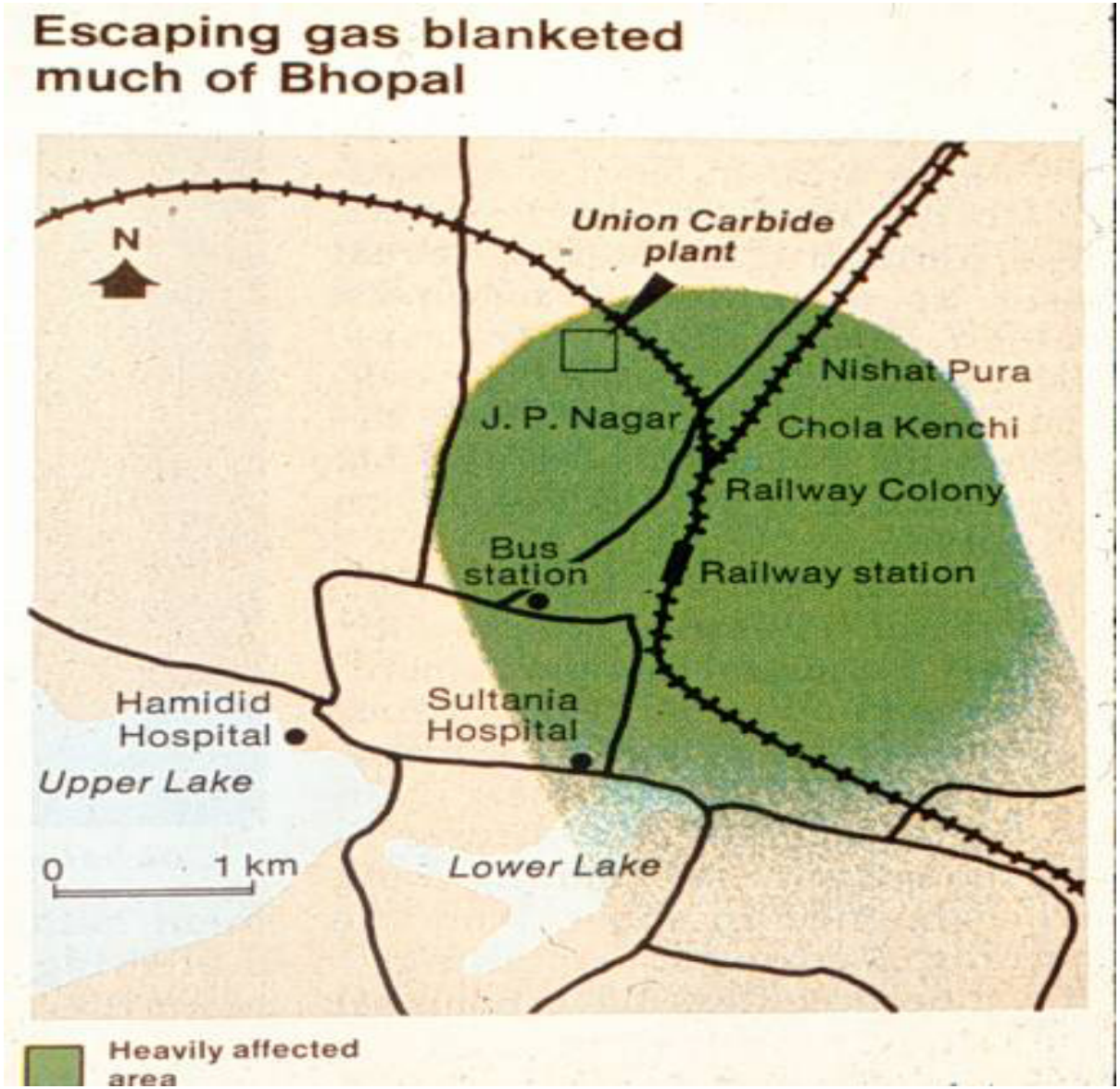
BHOPAL

Bhopal città con 1.400.000 ab. (attualmente) .

Si trova nello stato indiano del Madhya Pradesh (cioè quello cerchiato in rosso).



THE AFFECTED AREA



1984 - Bophal

THE POSSIBLE CAUSES

A tank containing methyl isocyanate (MIC) leaked.

MIC is an extremely reactive chemical and is used in production of the insecticide carbaryl.

The scientific reason for the accident was that water entered the tank where about **40 cubic meters of MIC** was stored.

When water and MIC mixed, an exothermic chemical reaction started, producing a lot of heat.

1984 - Bophal

THE POSSIBLE CAUSES

When water and MIC mixed, an exothermic chemical reaction started, producing a lot of heat.

As a result, the safety valve of the tank burst because of the increase in pressure.

It is presumed that between 20 and 30 tonnes of MIC were released during the hour that the leak took place.

The gas leaked from a 30 m high chimney and this height was not enough to reduce the effects of the discharge.

THE WEATHER EGGED ON THE PROCESS…

The high moisture content (aerosol) in the discharge when evaporating, gave rise to a heavy gas which rapidly sank to the ground.

A **weak wind** which **frequently changed direction**, which in turn helped the gas to cover more area in a shorter period of time (about one hour).

The weak wind and the weak vertical turbulence caused a slow dilution of gas and thus allowed the poisonous gas to spread over considerable distances.

1984 - Bophal

THE POSSIBLE REASONS…

One of the main reasons for the tragedy was found to be a result of a combination of human factors and an incorrectly designed safety system.

A portion of the safety equipment at the plant had been non-operational for four months and the rest failed.

UNION CARBIDE'S VERSION… (SABOTAGE)

" A disgruntled plant employee, apparently bent on spoiling a batch of methyl isocyanate, added water to a storage tank".

-------B. Browning Jackson

(Vice President)

1984 - Bophal

LAPSES ON THE PART OF THE GOVERNMENT

The Madhya Pradesh State government had not mandated any safety standards.

Union Carbide failed to implement its own safety rules.

The Bhopal plant experienced six accidents between 1981 and 1984, at least three of which involved MIC or phosgene.

UNION CARBIDES AMERICAN PLANT

Dr. Paul Shrivastava, an Associate Professor of Business in New York University conducted studies that revealed that Bhopal was neither an isolated incident nor the first of its kind in the corporation.

There had been many accidents of similar nature in UCC's American plants prior to the Bhopal accident.

He found that 28 major MIC leaks had occurred in UCC’s West Virginia plant during the five years preceding the Bhopal incident, the last one occurring only a month before.

1984 - Bophal

PROCESS CHEMISTRY

The reaction involved two reactants, methyl isocyanate (MIC) and alpha naphthol.

The process begins with a mixture of carbon – monoxide and chlorine to form phosgene. Phosgene is then combined with monomethylamine to form MIC. MIC is further mixed with naphthol to produce the end product carbaryl.

$$CO + Cl_2 \rightarrow COCl_2 \text{ (Phosgene)}$$

$$COCl_2 + CH_3NH_2 \rightarrow CH_3NHCOCl + HCl$$

$$CH_3NHCOCl \rightarrow HCl + CH_3NCO \text{ (Methyl Isoacyanate)}$$

1984 - Bophal

THE WATER WASHING THEORY

The media played a significant role in establishing the WATER WASHING THEORY as a plausible explanation.

According to this story, an MIC operator was told to wash a section of a subheader of the relief valve vent header ("RVVH") in the MIC manufacturing unit.

Because he failed to insert a **slip-blind**, as called for by plant standard operating procedures, the water supposedly backed up into the header and eventually found its way into the tank.

1984 - Bophal

THE WATER WASHING THEORY

Because he failed to insert a slip-blind, as called for by plant standard operating procedures, the water supposedly backed up into the header and eventually found its way into the tank and flowed **150 mt** to the tank which would require a **massive pressure head** and as indicated my reports would take **some time** to build up.

Conclusive reports indicated that 1000 kg of water entered the tank and for this water to build up and have an instantaneous exothermic reaction would not be possible

THE DIRECT-ENTRY THEORY

During the shift change -- that a disgruntled operator entered the storage area and hooked up one of the readily available rubber water hoses to Tank with the intention of contaminating and spoiling the tank's contents.

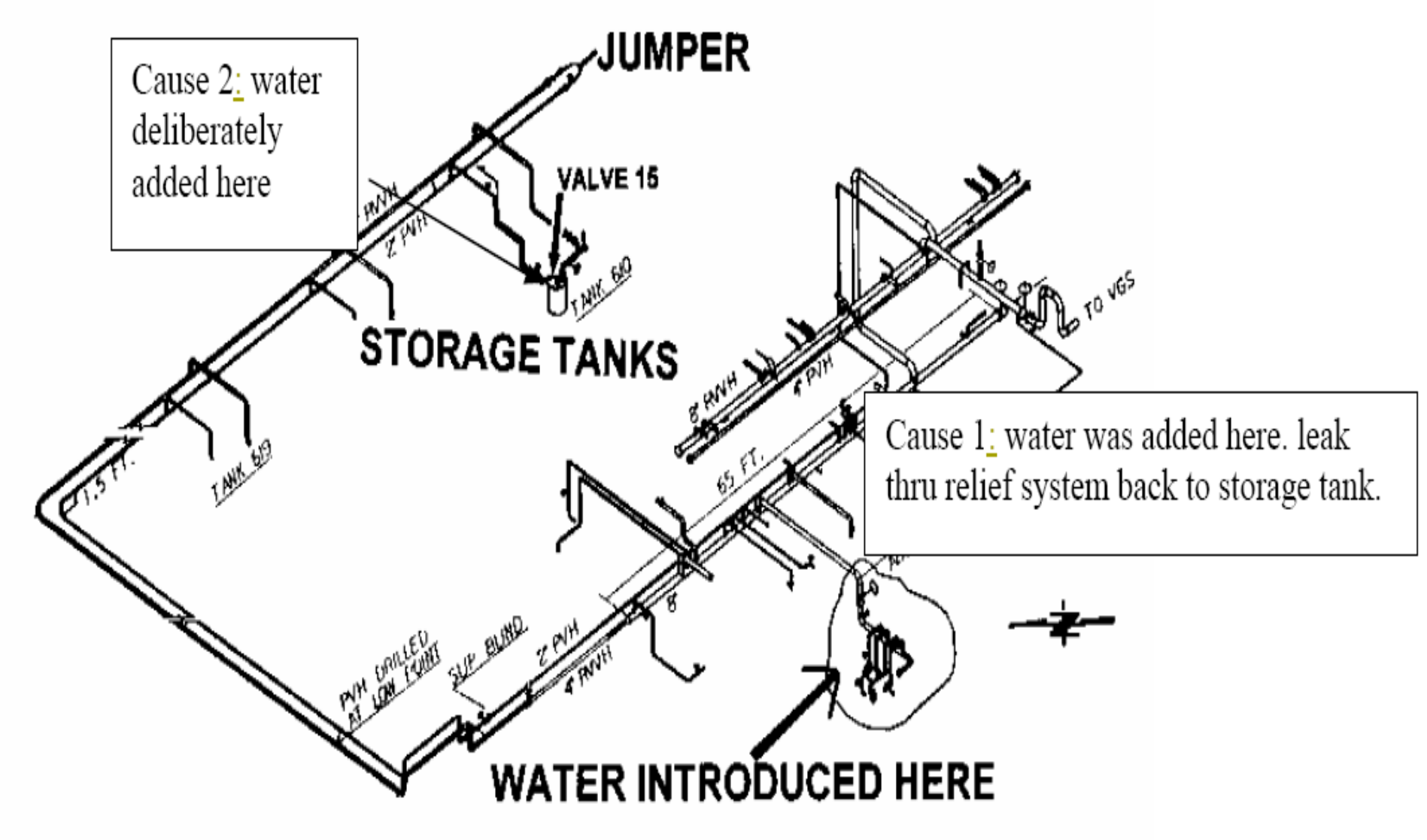
He unscrewed the local pressure indicator, which can be easily accomplished by hand, and connected the hose to the tank. The entire operation could be completed within five minutes.

1984 - Bophal

THE DIRECT-ENTRY THEORY

Minor incidents of process sabotage by employees had occurred previously at the Bhopal plant.

The water and MIC reaction initiated the formation of carbon dioxide which, together with MIC vapours, was carried through the header system and out of the stack of the vent gas scrubber by about 11:30 to 11:45 p.m


Cause 2: water deliberately added here
JUMPER
VALVE 15
STORAGE TANKS
TO VGS
Cause 1: water was added here. leak thru relief system back to storage tank.
WATER INTRODUCED HERE

1984 - Bophal

LAPSES ON PART OF UNION CARBIDE

Improper design of chimneys (without consideration of weather conditions in all seasons)

Improper design and maintenance of safety equipment.

Not following safety regulations as that followed by UCC plants in USA.

Decision to neglect a flare system in need of repair.

Inadequate emergency planning and community awareness.

Lack of awareness of the potential impact of MIC on the community by the people operating the plant.

Inadequate community planning, allowing a large population to live near a hazardous manufacturing plant.

1984 - Bophal

SAFETY CONSIDERATIONS ("LESSONS FROM DISASTER")

These principles would have averted the disaster.

Eliminate or reduce the production of Hazardous chemicals.

Hazardous chemicals produced should not be stored and should be consumed in the course of the reaction.

The inventory of Hazardous chemicals if inevitable should be of many small containers and not of one large container.

ALTERNATE CHEMISTRY (SUGGESTED SOLUTION)

Alpha Napthol on carbonyl group addition followed by reaction with methyl amine would eventually gives carbaryl.

This process does not generate or require handling the of Phosgene.

This process does not require storage of MIC.

Inherently safe process.

CONCLUSION

The Bhopal gas tragedy could have been averted.

There were lapses on part of the government and Union Carbide Company.

An alternate way to produce carbaryl was suggested.

Design of Inherently safer process was required.

CONSIDERAZIONI AGGIUNTIVE

Sebbene la vera dinamica resti ancora da stabilire è possibile fare qualche considerazione sull'incidente:

- presenza di un impianto altamente pericoloso in un'area densamente abitata
- assenza delle minime precauzioni richieste per trattare sostanze così tossiche
- mancanza pressocchè totale di formazione in merito alla sicurezza del personale
- assenza di "procedure sicure" e di misure di salvaguardia nel caso di incidente
- occorre considerare sempre la possibilità di un errore umano ed evitare che ciò porti ad un disastro

1984 - Bophal

1984 - THE TRAGEDY OF SAN JUANICO, PEMEX, MEXICO CITY

Summary of damages:

550 people killed.

2,000 people receive severe burns.

7,231 people classed as injured.

PEMEX PLANT

Pemex is a liquid petroleum gas (LPG) distribution plant.

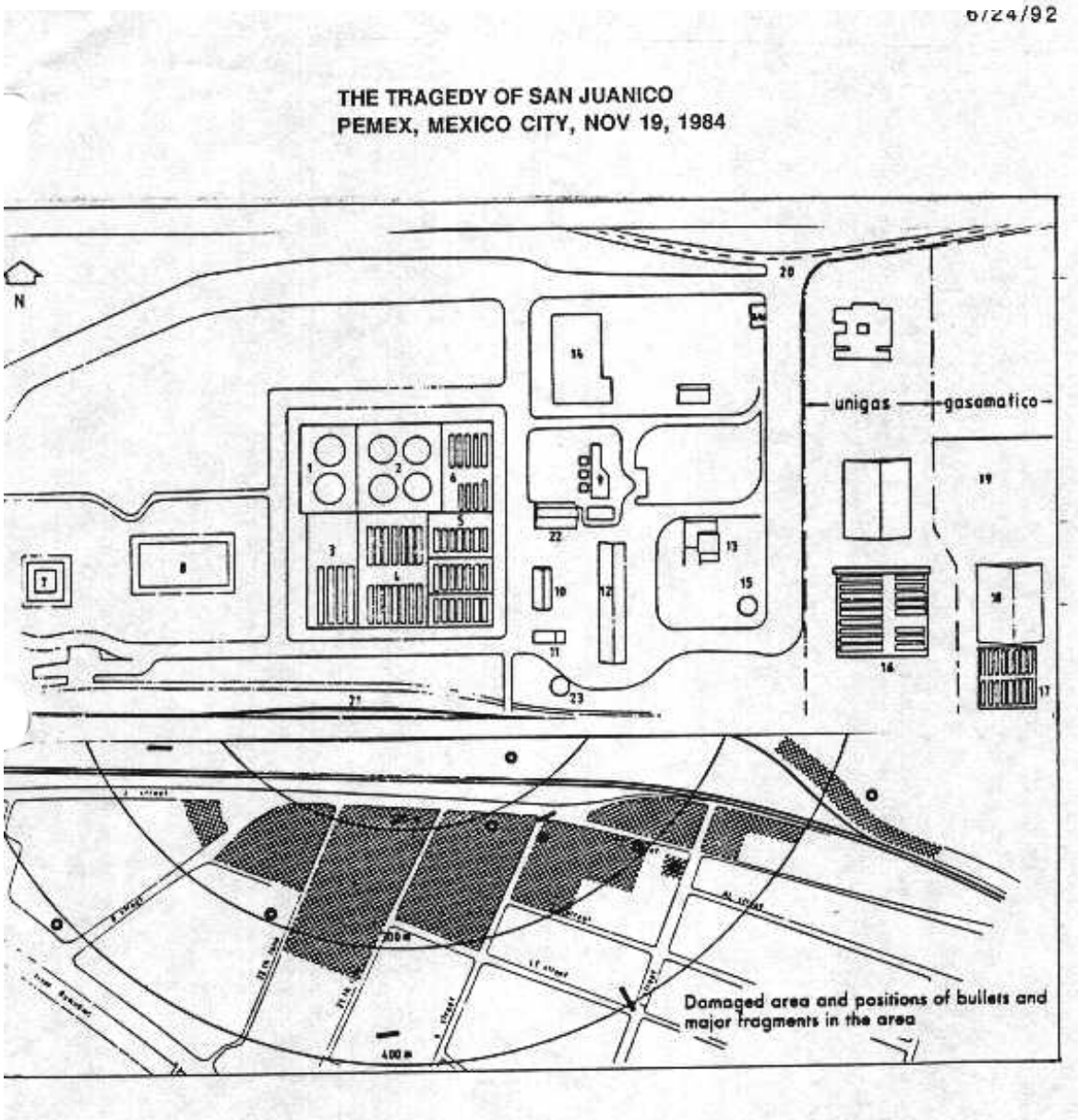
Total storage capacity: more than 11000 cubic meters of LPG

Pemex is located a few km. north of Mexico City .

Plant was 25 years old and built to 1950 API standards of the U.S.

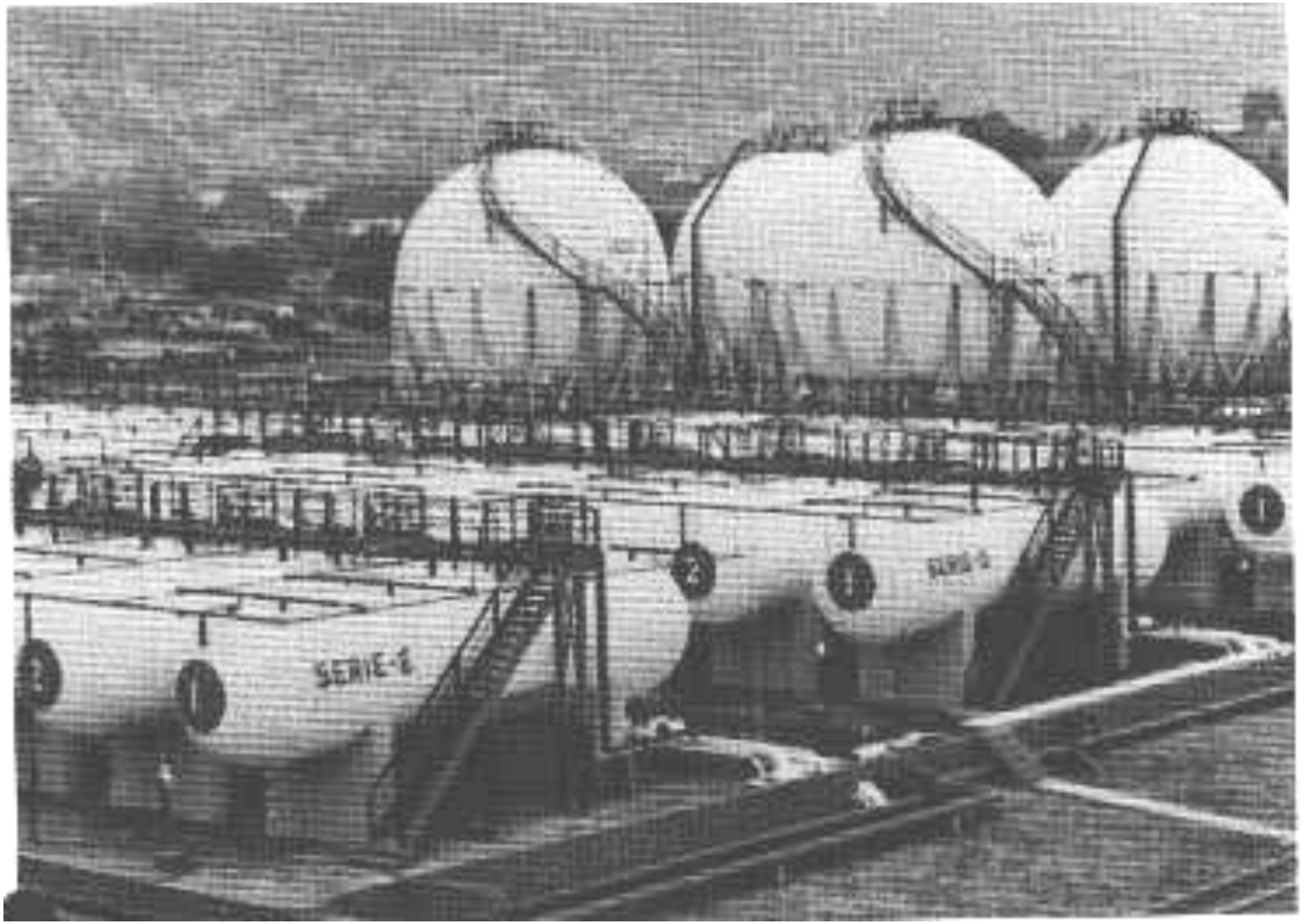
1984 - PEMEX, Mexico City

PEMEX PLOT PLAN - BEFORE



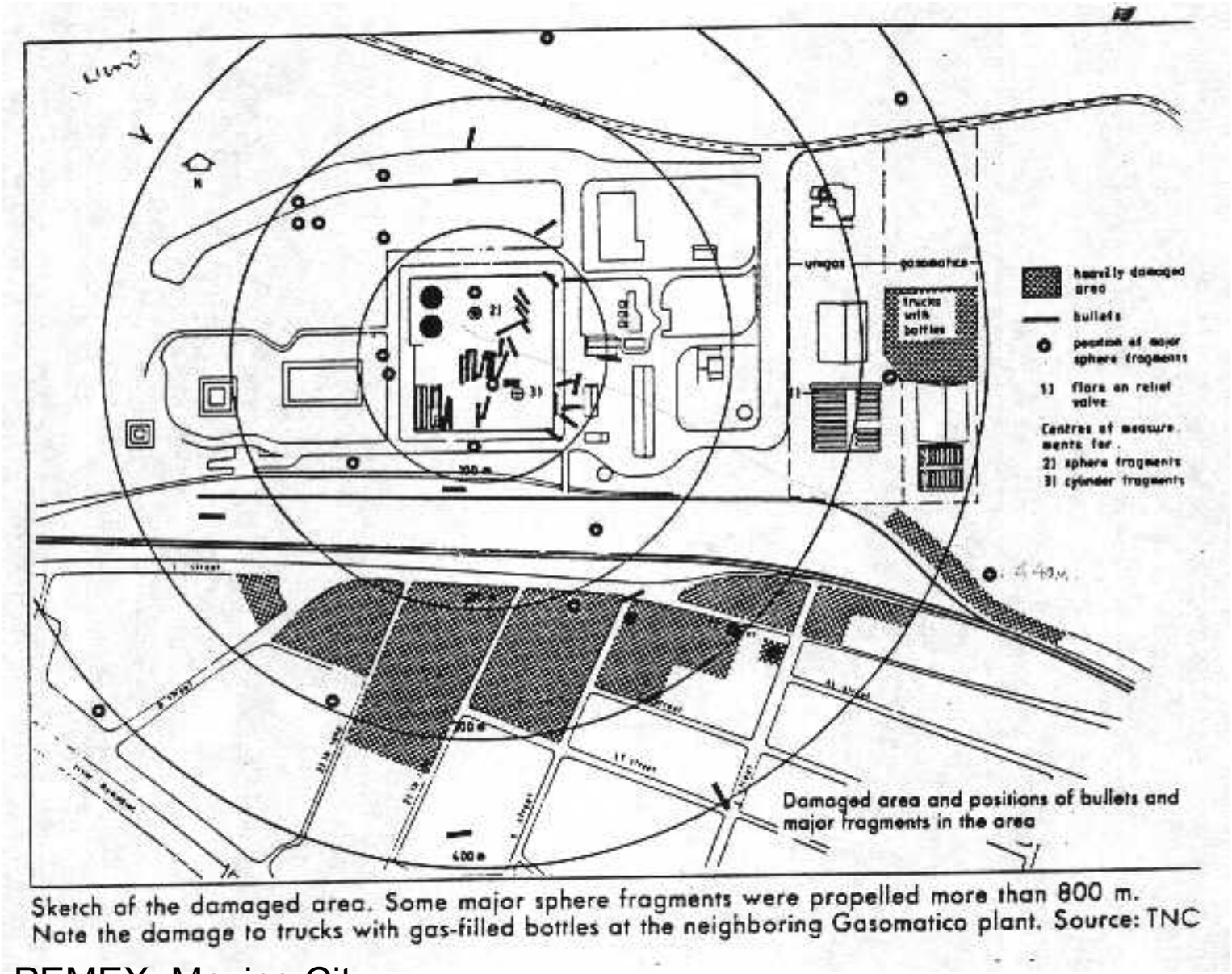
1984 - PEMEX, Mexico City

PEMEX BEFORE BLEVES



1984 - PEMEX, Mexico City

PLOT PLAN - AFTER



Sketch of the damaged area. Some major sphere fragments were propelled more than 800 m. Note the damage to trucks with gas-filled bottles at the neighboring Gasomatico plant. Source: TNC

1984 - PEMEX, Mexico City

INITIATING EVENT

Emergency Block Valve shuts feed to a sphere at 90% full.

Possible “water hammer” damages the 8 in. feed pipe near the vapor phase of F-4.

Vapor cloud drifts toward a ground flare, ignites and causes a **flash fire**.

The flame burns back to source and impinges on vapor space of sphere F-4.

10 minutes after line rupture, sphere F-4 BLEVEs (*Boiling Liquid Expanding Vapor Explosion*).

1984 - PEMEX, Mexico City

INITIATING EVENT

Vessel explosion as pressure is relieved (domino effect).

Fire ball from flashing contents.

Large energy release breaks vessel into pieces which fly off as missiles.

Missiles from F-4 strike other vessels (domino effect).

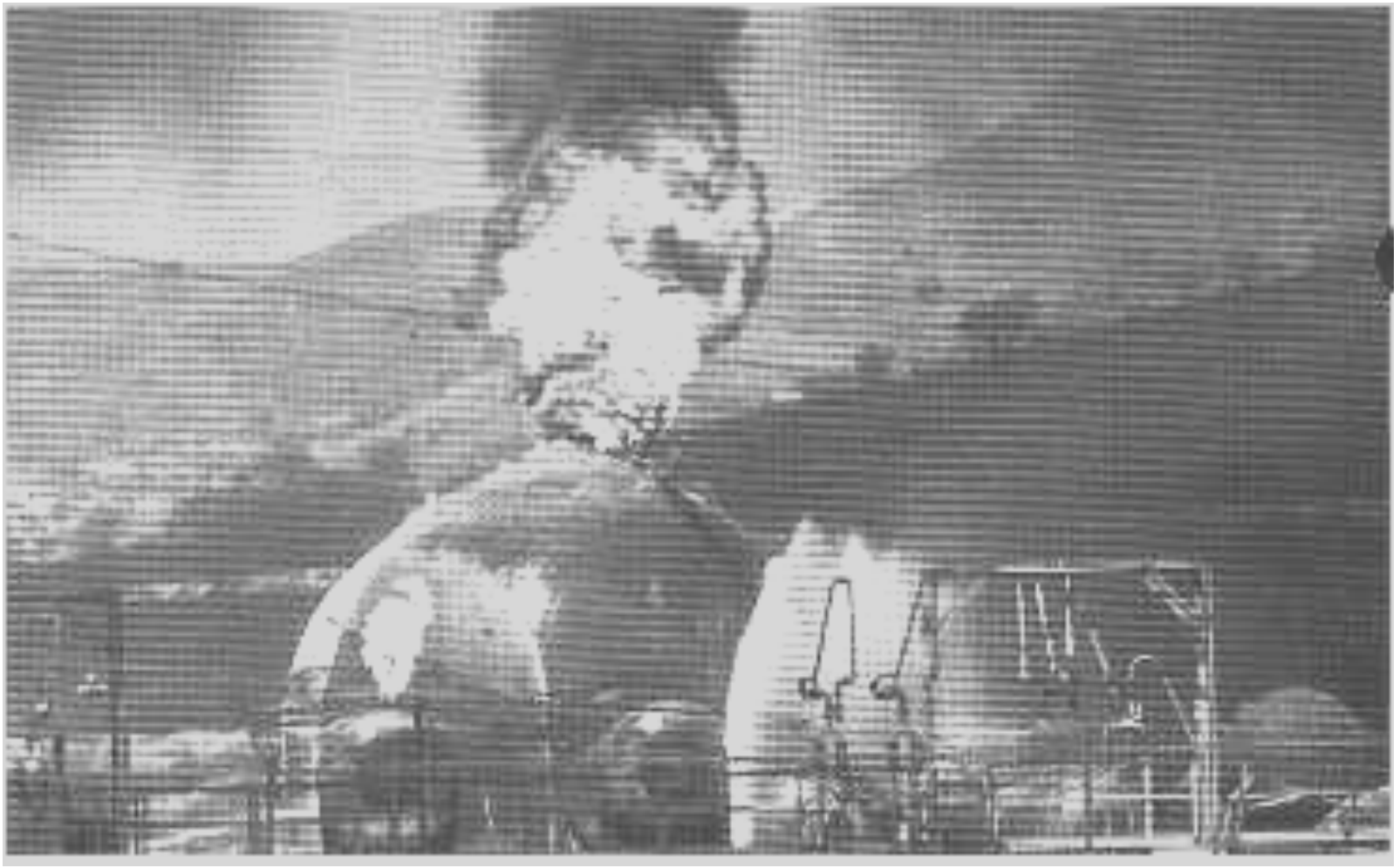
More liquid leaks, more fires and other BLEVEs are created (domino effect).

14 other vessels BLEVE in domino fashion over a 5 hour period.

The site emergency fire water system is overwhelmed.

1984 - PEMEX, Mexico City

F-4 FAILURE



1984 - PEMEX, Mexico City

BULLET TANK AREA

1984 - PEMEX, Mexico City

NEARBY HOUSES

The desolation of the burnt-out houses recalled a war scene.

1984 - PEMEX, Mexico City

MISSILE ALERT

F1, F2, F3 and F4 spheres **disappear**.

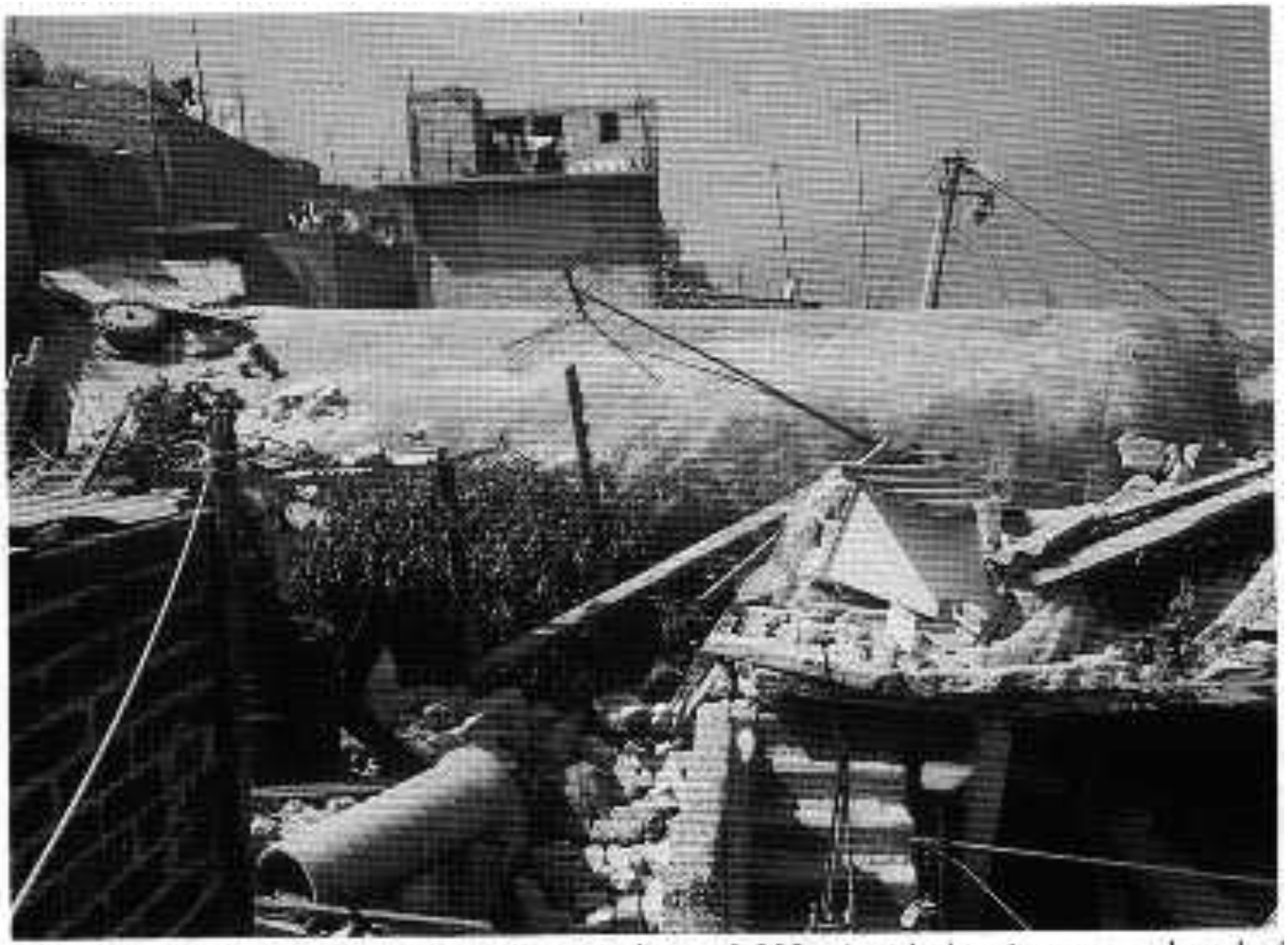
Avg. wt. of a bullet vessel was **20 tons**.

Furthest missile traveled **1,200 meters**.

Burning HCs rained on neighboring village 130 m from fence line.

1984 - PEMEX, Mexico City

MAXIMUM MISSLE



The cylindrical tank that flew furthest penetrated some 1,200 m into the housing area and crashed into a 2 storey house vacated one hour before.

1984 - PEMEX, Mexico City

EMERGENCY RESPONSE

First firefighters arrive 15 minutes after F-4 **BLEVE**.

100 ambulances and 200 firefighters involved.

985 medics and 1,780 paramedics involved.

1,332 medical volunteers in 33 hospitals involved.

1984 - PEMEX, Mexico City

LESSONS LEARNED

Old plant, too congested, poor maintenance & poor operator training were cited.

Village should have been 1,500 meters from terminal (determined by QRA analysis).

Require many gas detectors and alarms.

Emergency Block Valve closure rates need adjustment.

Emergency plan required.

1984 - PEMEX, Mexico City

LA LEZIONE FINALE

Molti incidenti accadono non perchè

non sappiamo

come prevenirli ma perchè

non abbiamo usato la conoscenza

che era già disponibile.

Questa è, in ultima analisi, la lezione!