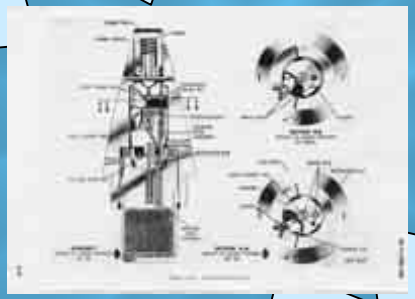
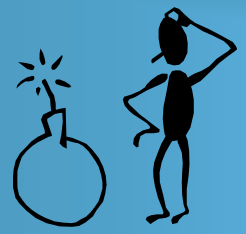
AN OVERVIEW OF EXPLOSIVES WITH EMPHASIS ON PRIMARY OR INITIATING EXPLOSIVES





GOALS

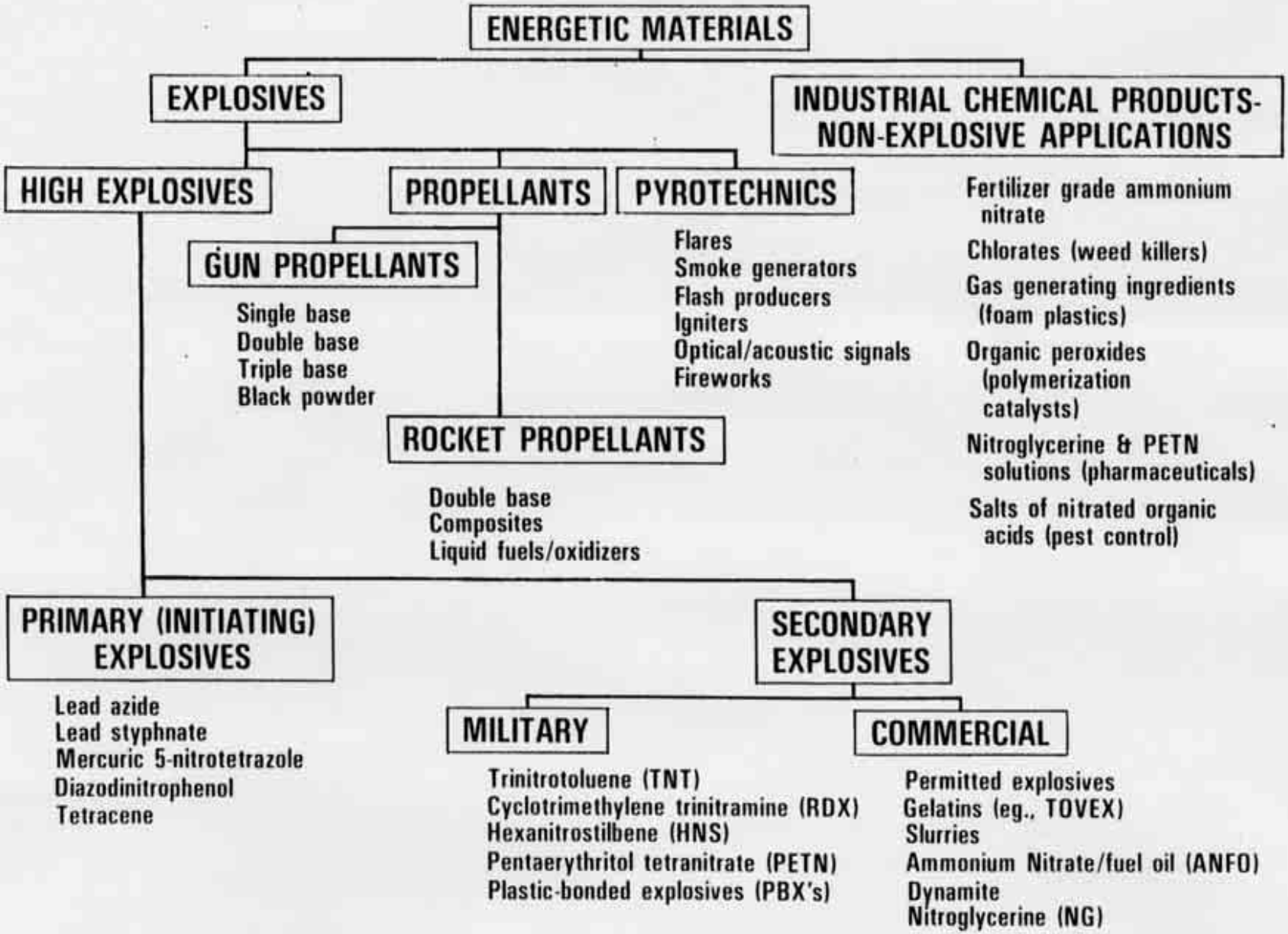
Put Primary [Initiating High Energetic Compounds] Explosives into Perspective with respect to HTRW Initiatives.

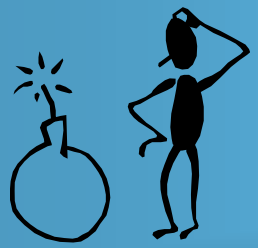
Present Analytical Results from the Azide Screening Initiative at the Ravenna Army Ammunition Plant

Present the "Understanding the Manufacturing Process Concept" for Technical Process Planning of HTRW Initiatives.

Examine some common deactivation process used in the Munitions Industry for Initiating and Secondary Explosives.

EXAMPLES OF TYPES OF ENERGETIC MATERIALS AND SOME APPLICATIONS





INITIAL OBJECTIVE

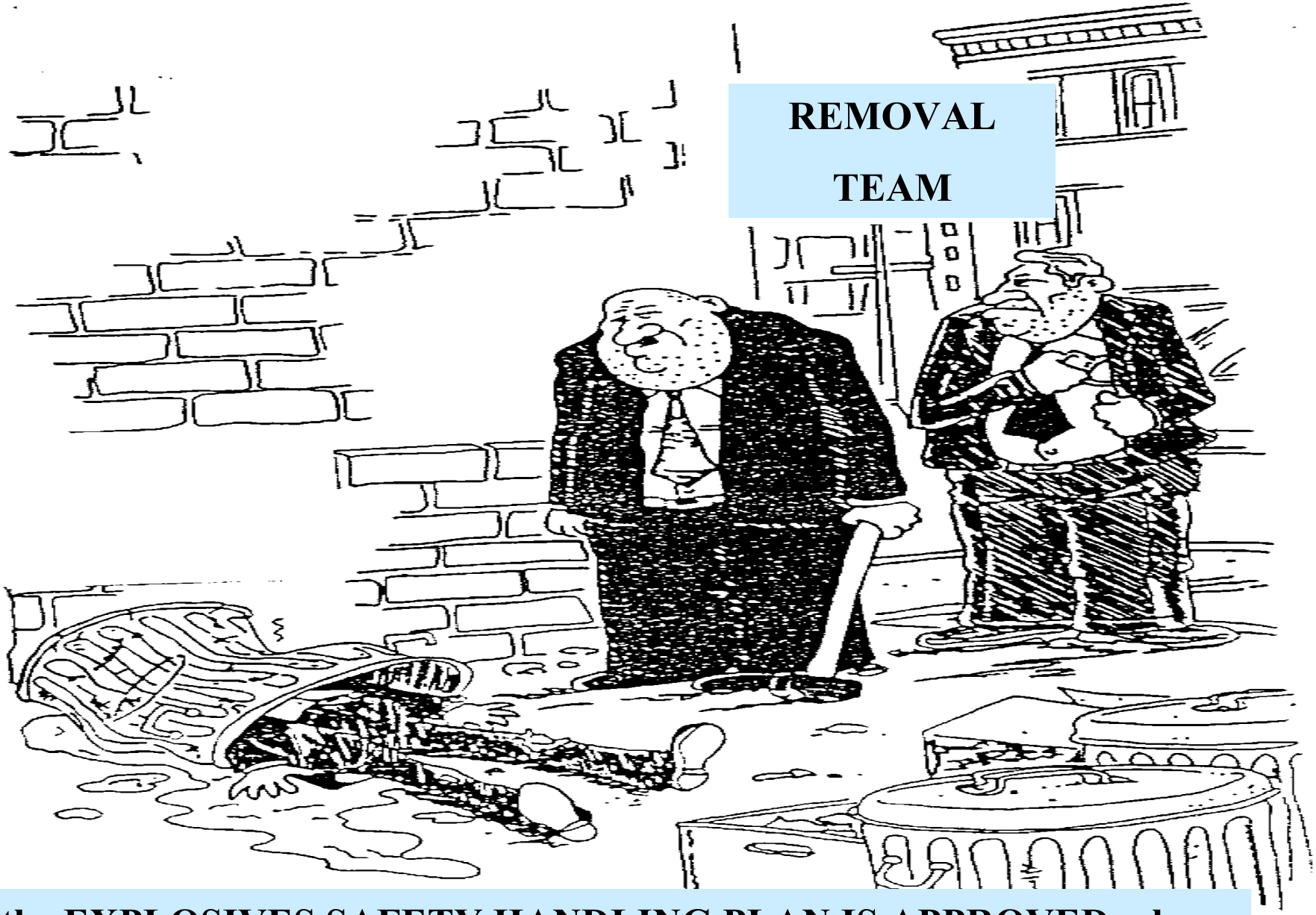
Putting

Primary

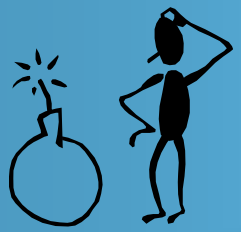
Explosives

Into

Persp



If the EXPLOSIVES SAFETY HANDLING PLAN IS APPROVED, please disregard this notice!



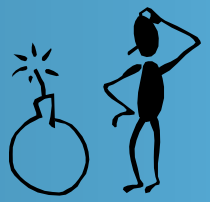
IGNITION STIMULUS

IMPACT

HEAT

FRICTION

ELECTROSTATIC DISCHARGE



TYPES OF LEAD AZIDE

CHARACTERISTIC	DEXTRINATED	RD1333	PVA	BRITISH	
				SERVICE	COLLOIDAL
LEAD AZIDE, %	92.8	98.7	96.0	98.1	99.9
TOTAL LEAD, %	69.3	71.06	71.6	71.5	71.67
PARTICLE SIZE AVERAGE, MICRONS	24.5	34.5	19.0	55.0	3.4

IMPACT SENSITIVITY

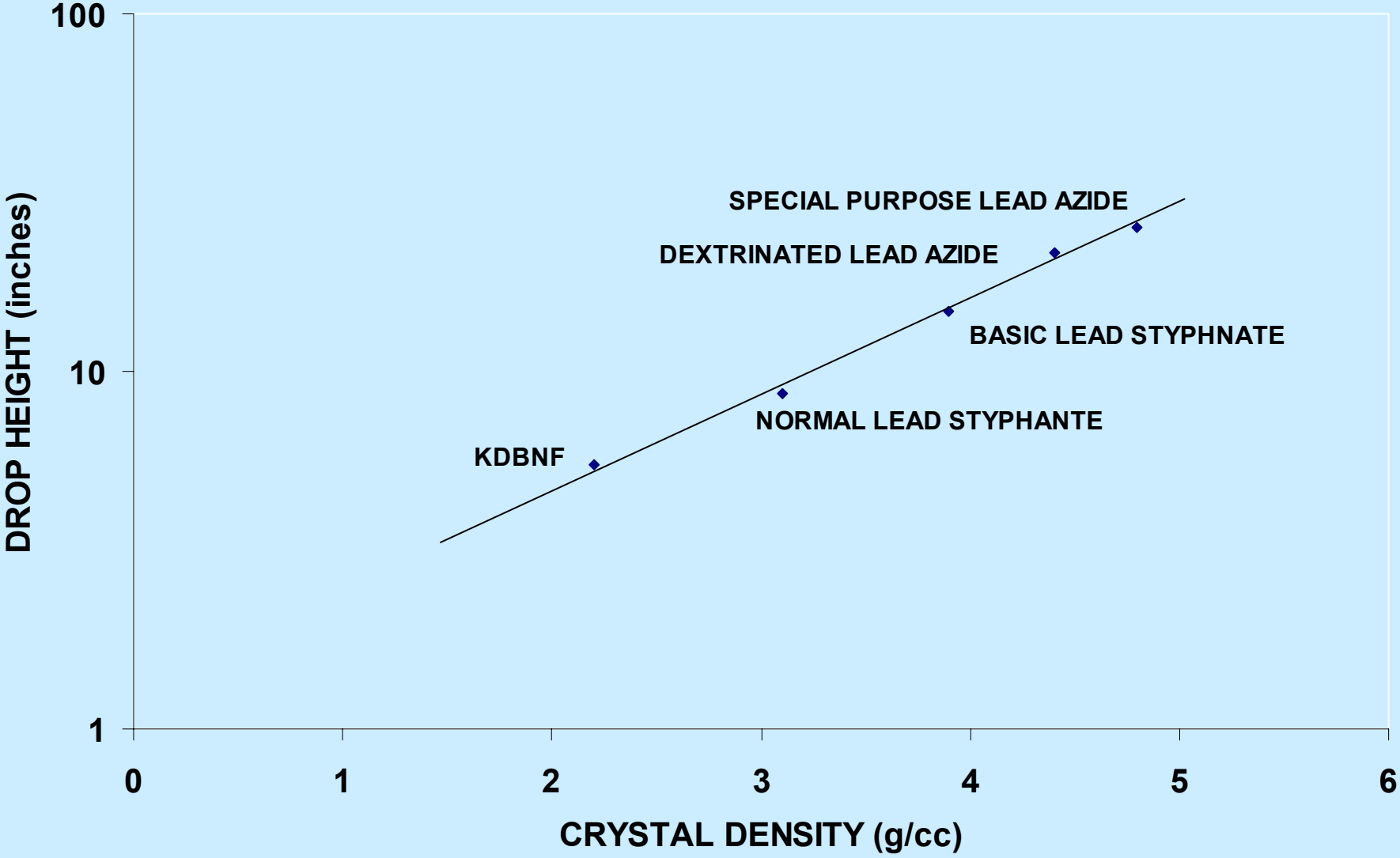
US BUREAU OF MINES

2 Kg Weight, 20 mg Sample

Explosive	Min. Ht (cm)
Mercury Fulminate	5
Nitrocellulose	8
Lead Azide	10
Nitroglycerin	15
Lead Azide (Dext)	17
Lead Styphnate	17
PETN	17
Tetryl	26
Black Powder	32
RDX	32
HMX	32
Pentolite *	65
TNT	95 – 100 +
Comp. C4 **	100 +
Ammonium Nitrate	100 +

* 90% TNT, 10% PETN
** 91% RDX, 9% Plasticizer

IMPACT SENSITIVITY PLOT



IMPACT TESTING APPARATUS

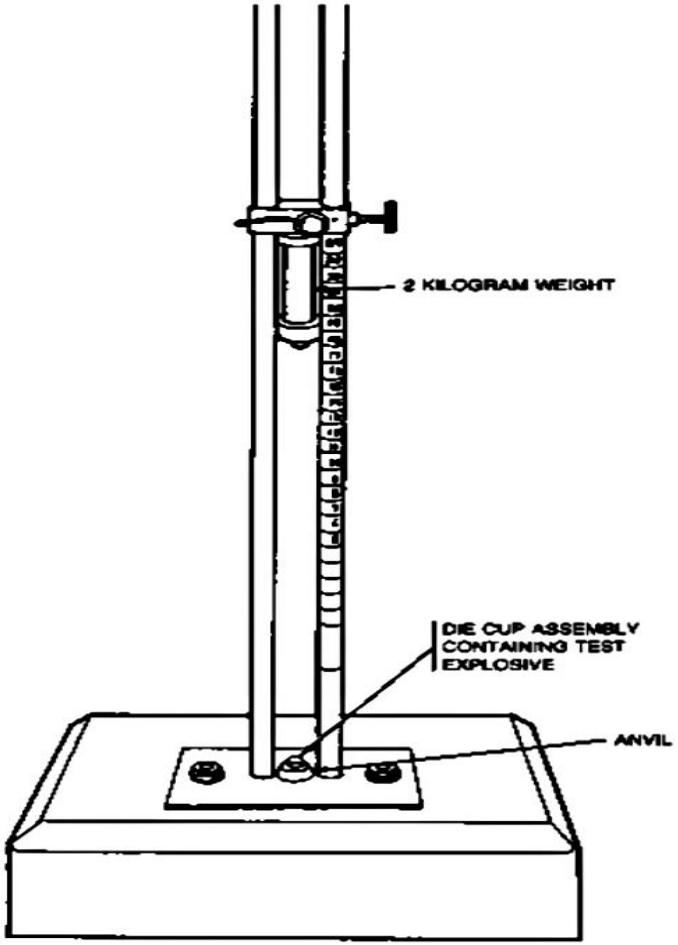


Figure 5-4. Picatinny Arsenal impact test apparatus.

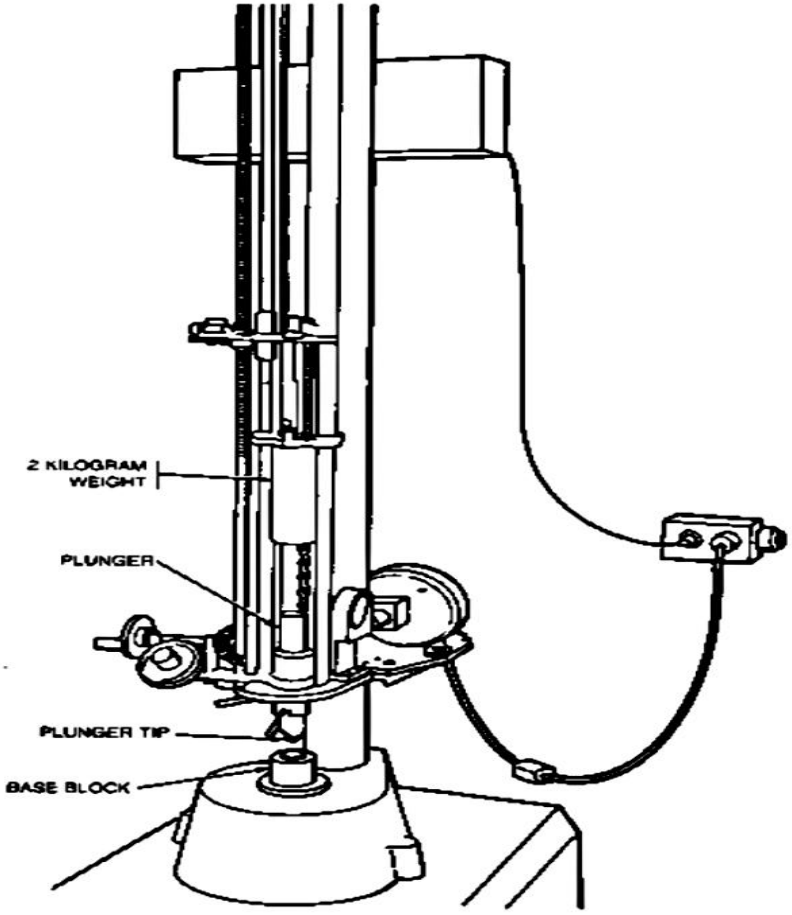
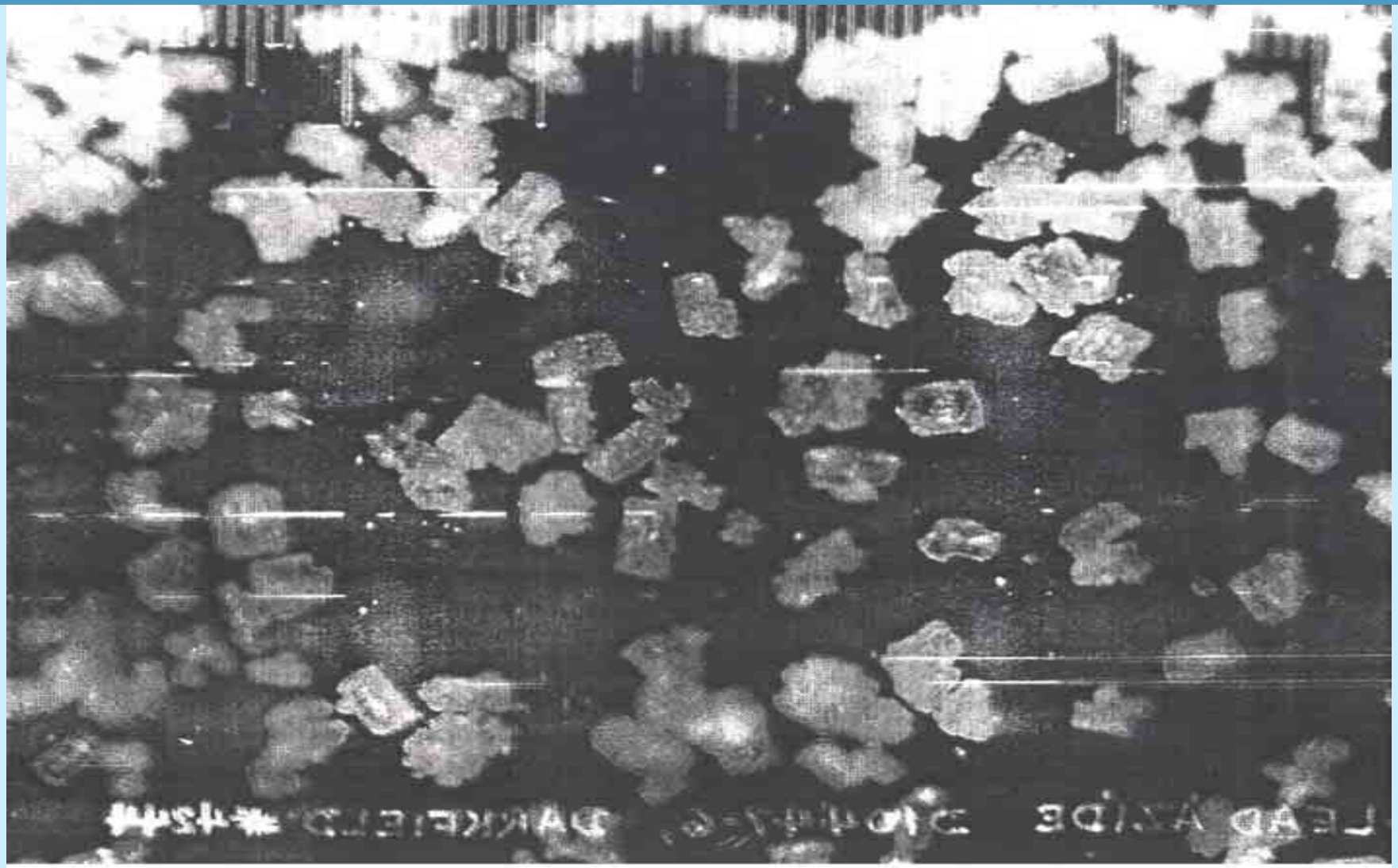


Figure 5-6. Bureau of Mines impact test apparatus.

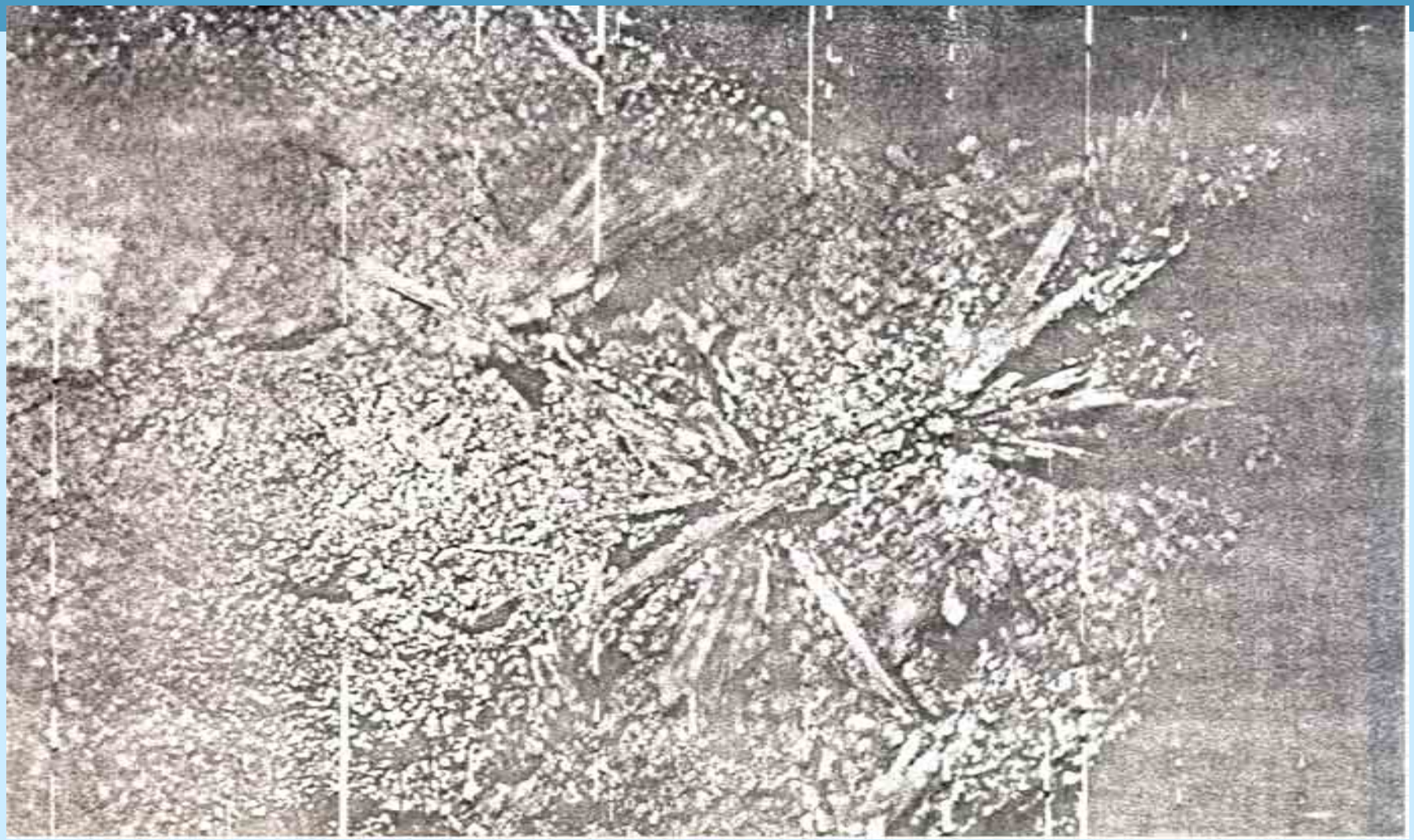
Dextrinated Lead Azide



LEAD AZIDE GEODES

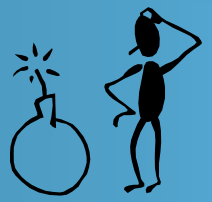
Lead Styphnate, Normal

Lead Styphnate, Monoclinic



FRICTION SENSITIVITY

EXPLOSIVE	BAMS FRICTION 50% INITIATION LEVEL g	BAMS SENSITIVITY 10% INITIATION LEVEL g	DTA ACTIVATION ENERGY Kcal/mole	AUTOIGNITION TEMPERATURE C	BALL DROP IMPACT SENSITIVITY VALUES 50% HEIGHT inches	CRYSTAL DENSITY g/cc
COLLOIDAL LEAD AZIDE	15 +/- 7		40	257		4.8
PVA LEAD AZIDE	50+/-22	10				4.8
SPECIAL PURPOSE LEAD AZIDE			36	280	22.4+/-2.1	4.8
RD 1333 LEAD AZIDE	81+/-29	20	41	287	20.1+/-3.5	
DEXTRINATED LEAD AZIDE	157+/-50	100	44	284	21.5+/-3.3	4.4
BASIC LEAD STYPHNATE	250+/-100	40	40	235	14.7+/-4.4	3.9
NORMAL LEAD STYPHNATE	285+/-200	100	40	249	8.7+/-1.6	3.1
KDBNF	400+/-100	50	38	180	5.5+/-2.2	2.2
TETRAZENE	850+/-250	300	55	122		1.7
60/40 NORMAL LEAD STYPHNATE/POTASSIUM PERCHLORATE	1400+/-600	600				
NOL 130	1350+/-100	800	45	236	7.2+/-2.7	
PA 100	325+/-100	200				



ELECTROSTATIC SENSITIVITY

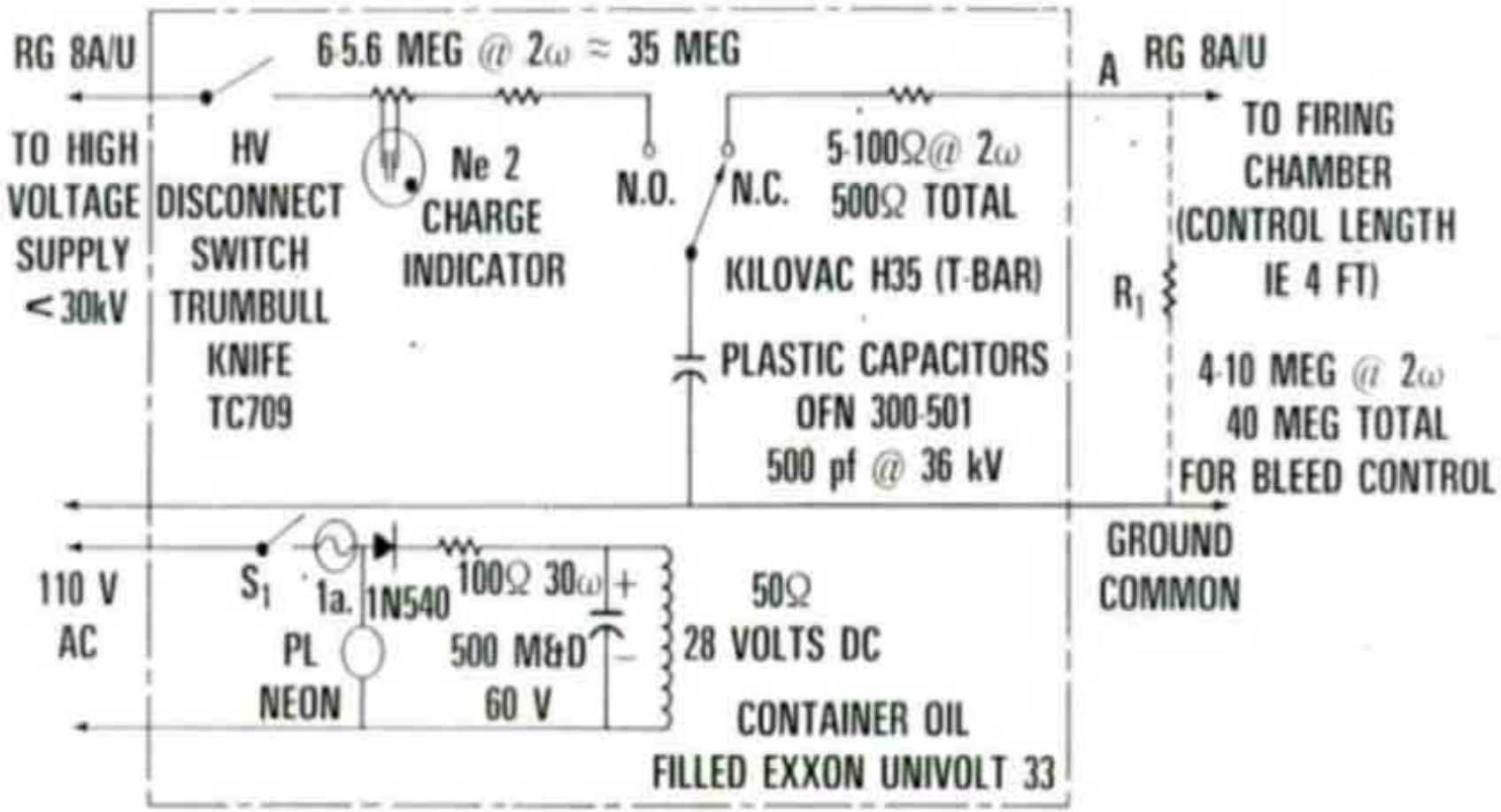
	IMPACT SENSITIVITY	ELECTROSTATIC SENSITIVITY		
	50% Ht (CM)	CAPACITANCE (uFd)	POTENTIAL (VOLTS)	MAX. NO-FIRE ENERGY LEVEL mJ
(A) MILLED DXW-1, CERAMIC	5.9	1.0	500	125
(B) MILLED DXW-1, STEEL	5.6	1.0	400	80
(C) UNMILLED DXW-1	7.8	1.0	750	280
(D) NORMAL LEAD STYPHNATE	8.8	1.0	350	61
(E) DEXTRINATED LEAD AZIDE	3.4	1.0	1000	500

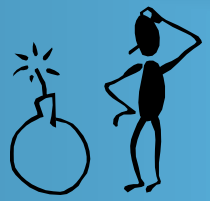
TEST PARAMETERS

1. IMPACT SENSITIVITY - BRUCETON TYPE TEST, 25 SHOTS/SAMPLE, 35 MG LOOSE UNCONFINED EXPLOSIVE/SHOT, 2.5 KG DROP WEIGHT

2. ELECTROSTATIC SENSITIVITY - METAL/RUBBER ELECTRODE SYSTEM, MAXIMUM NO-FIRE LEVEL BASED ON 20 CONSECUTIVE TRIALS WHERE NO INITIATIONS ARE OBSERVED

ELECTROSTATIC DISCHARGE TEST SET SCHEMATIC





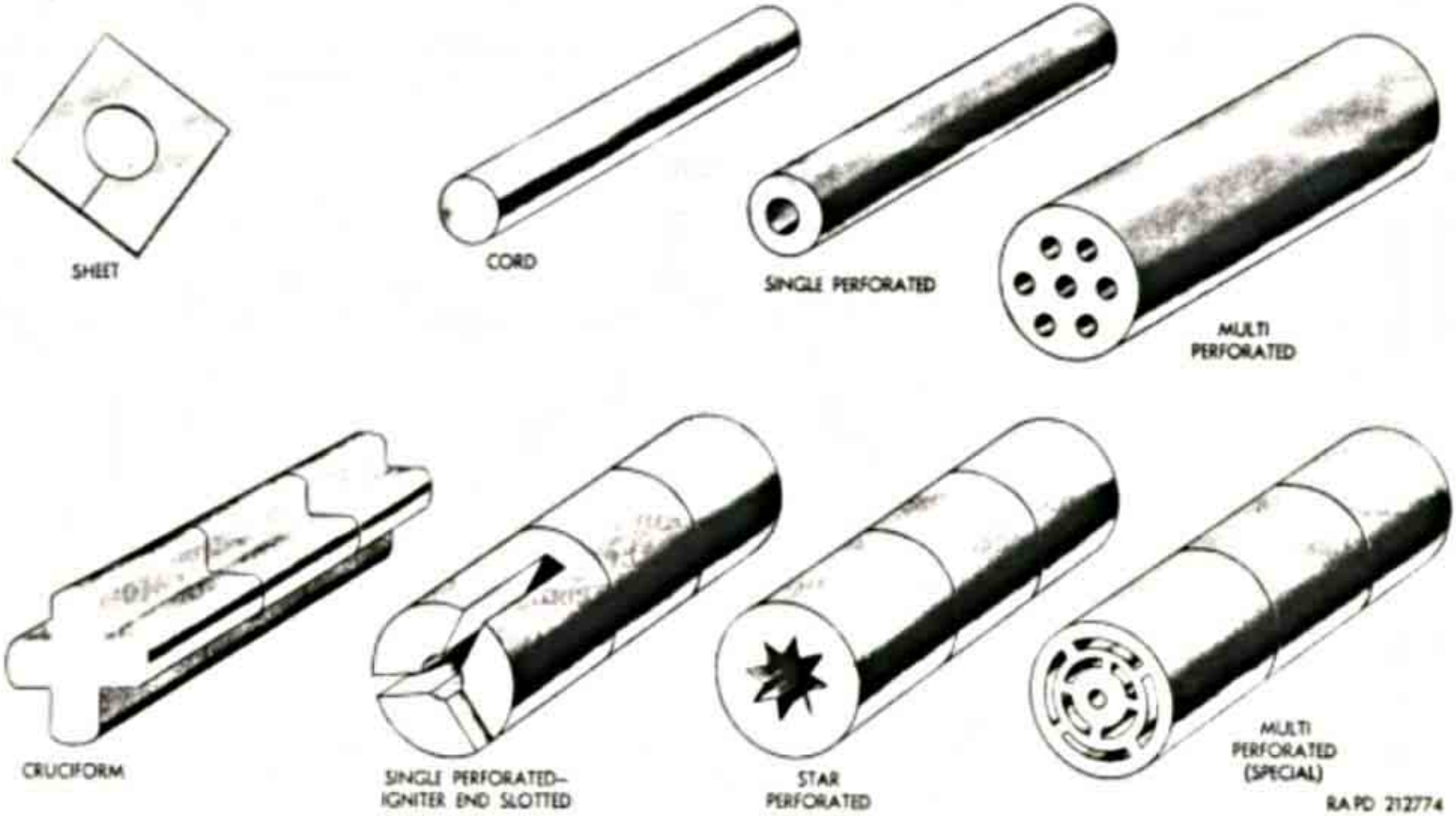
GUN PROPELLANTS

Composition	M1	M2	M3	M4	M5	M6	M7	M8	M9	M10	M12	M13	M14
	Percent												
Nitrocellulose													
12.60 % N			79										
13.15 % N	84					86	55			98	98	57	89
13.25 % N		76		76	82			52	58				
Nitroglycerin		20			15		36	43	40			40	
Barium Nitrate		1.5			1.5								
Potassium Nitrate		1			1			1.3	1.5				
Potassium Perchlorate							7.8						
Nitroguanidine													
Dinitrotoluene	9.9	1		23		9.9					9		7.9
Trinitrotoluene			15										
Dibutylphthalate	4.9					3							2
Diethylphthalate								3					
Triacetin			5										
Potassium Sulfate										1	0.8	1.5	
Tin											0.8		
Diphenylamine	1	0.8	1	1	0.8	1			0.8	1	0.8	0.2	1
Ethyl Centralite							0.9	0.6				1	
Graphite		0.3			0.3								
Carbon Black							1.2					0.1	

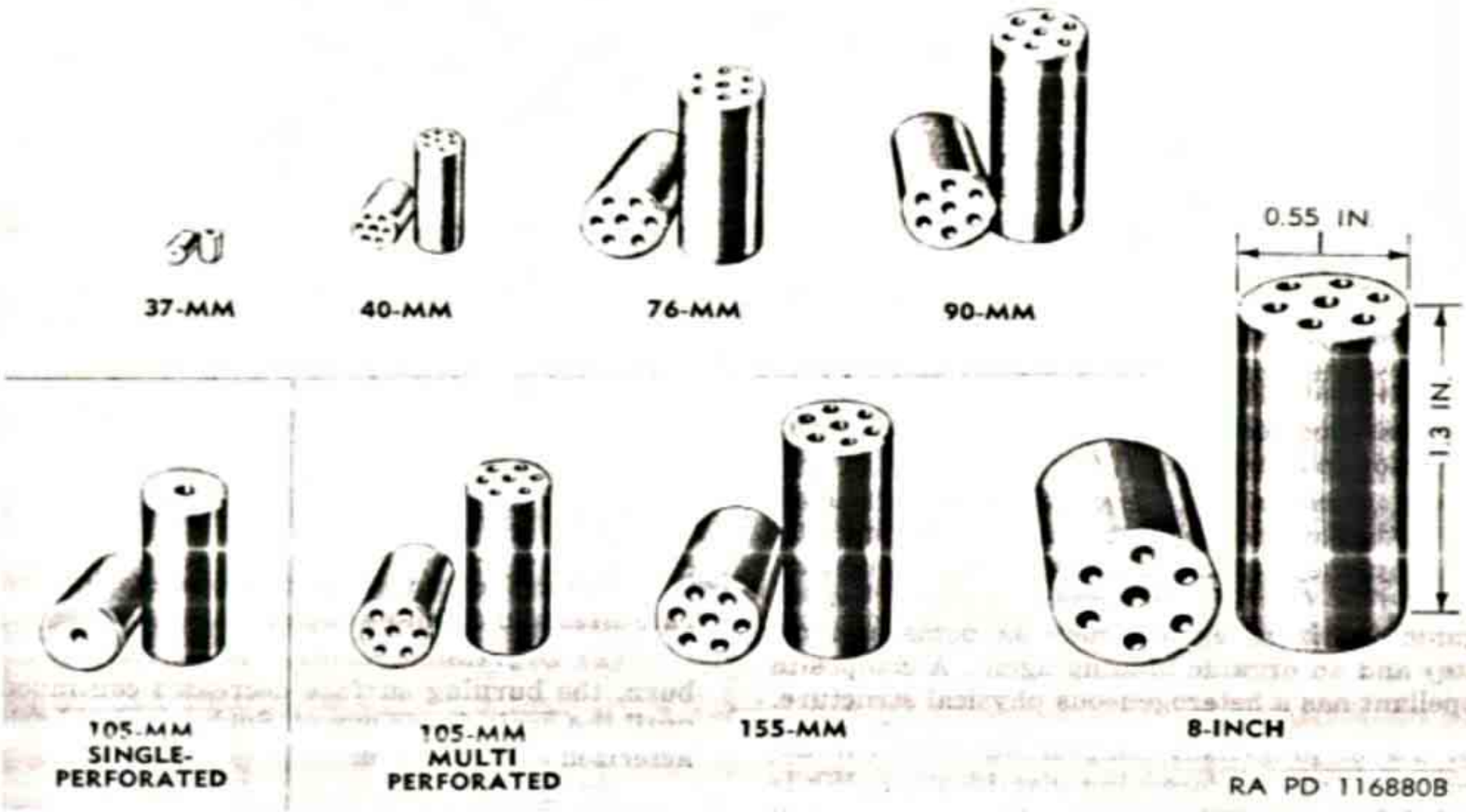
ROCKET PROPELLANTS

Composition	T2	T3	T5	T6	T8	T9
	Percent					
Nitrocellulose						
12.20 % N		56		55.5		
13.15 % N	58		57.5		58	
Nitroglycerin	30	27	39.2	27.5	22.5	49.8
Potassium Nitrate						
Dinitrotoluene	2.5	9.3		10.5	2.5	40.7
Explosive "D" Ammonium Picrate						
Triacetin					8.5	
Potassium Sulfate	1.5		1.5	1.5		
Methyl Cellulose		0.11				
Ethy Cellulose						4.5
Ethyl Centralite	8	7.2	1.75	4	8	
Carbon Black	0.02		0.05	0.5		
Lead Stearate or Lead Salicylate		0.5	0.1	0.5	0.5	
Calcium Stearate						0.5
Chlorinated Wax						4.5

PROPELLANT SHAPES

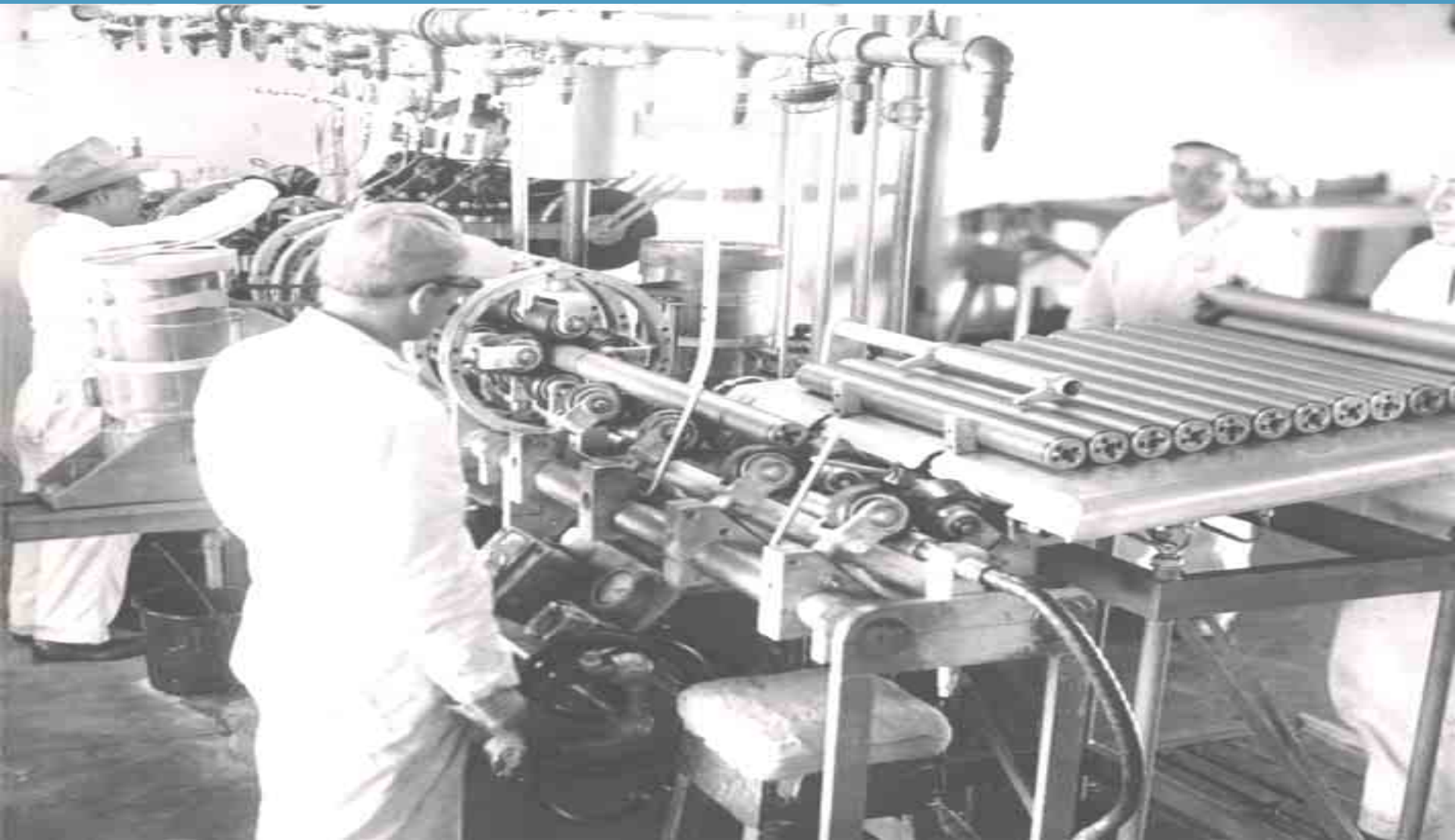


PROPELLANT SIZES



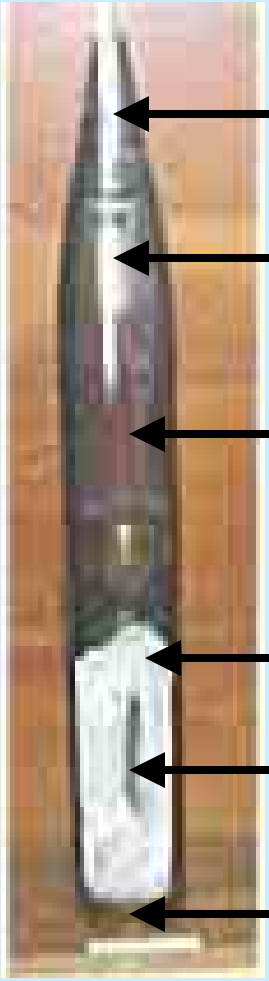
ROCKET PROPELLANT SUNFLOWER AAP

MK 43 ROCKET MOTORS SUNFLOWER AAP



KSAAP PRODUCTS

105 MM BREAKDOWN



- Fuze
  - Detonator → 93 mg Lead Azide
  - Percussion Element → 159 mg
- Booster Charge → 23 grams of Tetryl
- Main Charge → 5 lbs Comp B or TNT
- Propellant Charge → Lbs/Variable
- Primer → 300 gm Black Powder
- Percussion Element → 65 mg

KIM'S RULER

PERCUSSION ELEMENT CLOSEUP

Primer Mix Compositions

Component	FA874	FA956	FA70	FA90A
Antimony Sulfide	-----	15.0	17.0	12.0
Potassium Chlorate	-----	-----	53.0	53.0
Barium Nitrate	44.25	32.0	-----	-----
Calcium Silicide	13.0	-----	-----	-----
Lead Styphnate	40.0	37.0	-----	-----
Lead Thiocynate	-----	-----	25.0	25.0
Tetracene	-----	4.0	-----	-----
PETN	-----	5.0	-----	10.0
Aluminum Powder	-----	7.0	-----	-----
Acetylene Black	0.75	-----	-----	-----
TNT	-----	-----	5.0	-----
TNR	1.00	-----	-----	-----
Gum Arabic	1.00	-----	-----	-----

Buildings AP-2 & 3

[AP-2 Staging Storage & AP-3 Black Powder Screening]

Building AP-3 Interior
[Black Powder Screening Operation]

Artillery Primer Line Sump Removal

AP SUMP REMOVAL RVAAP

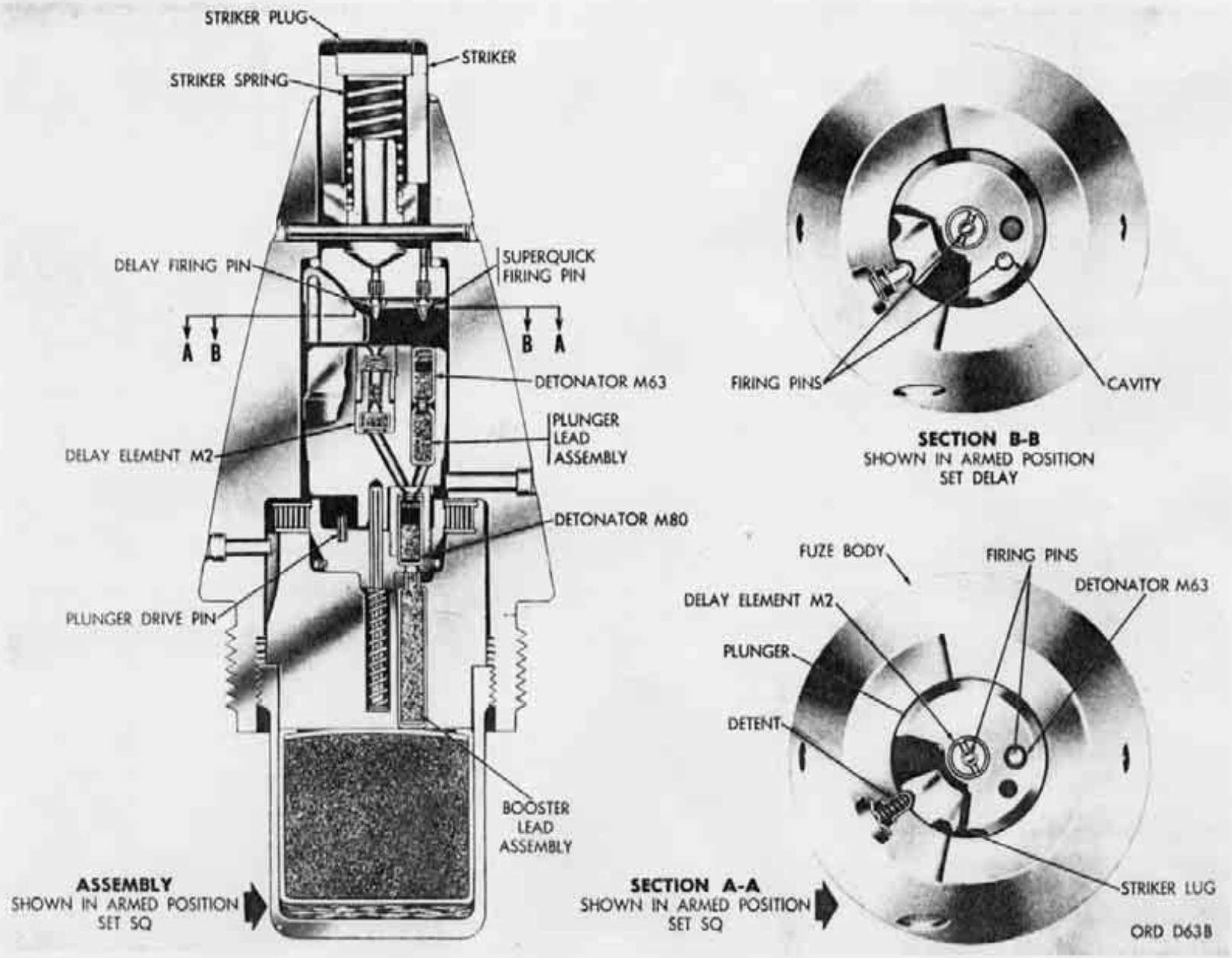
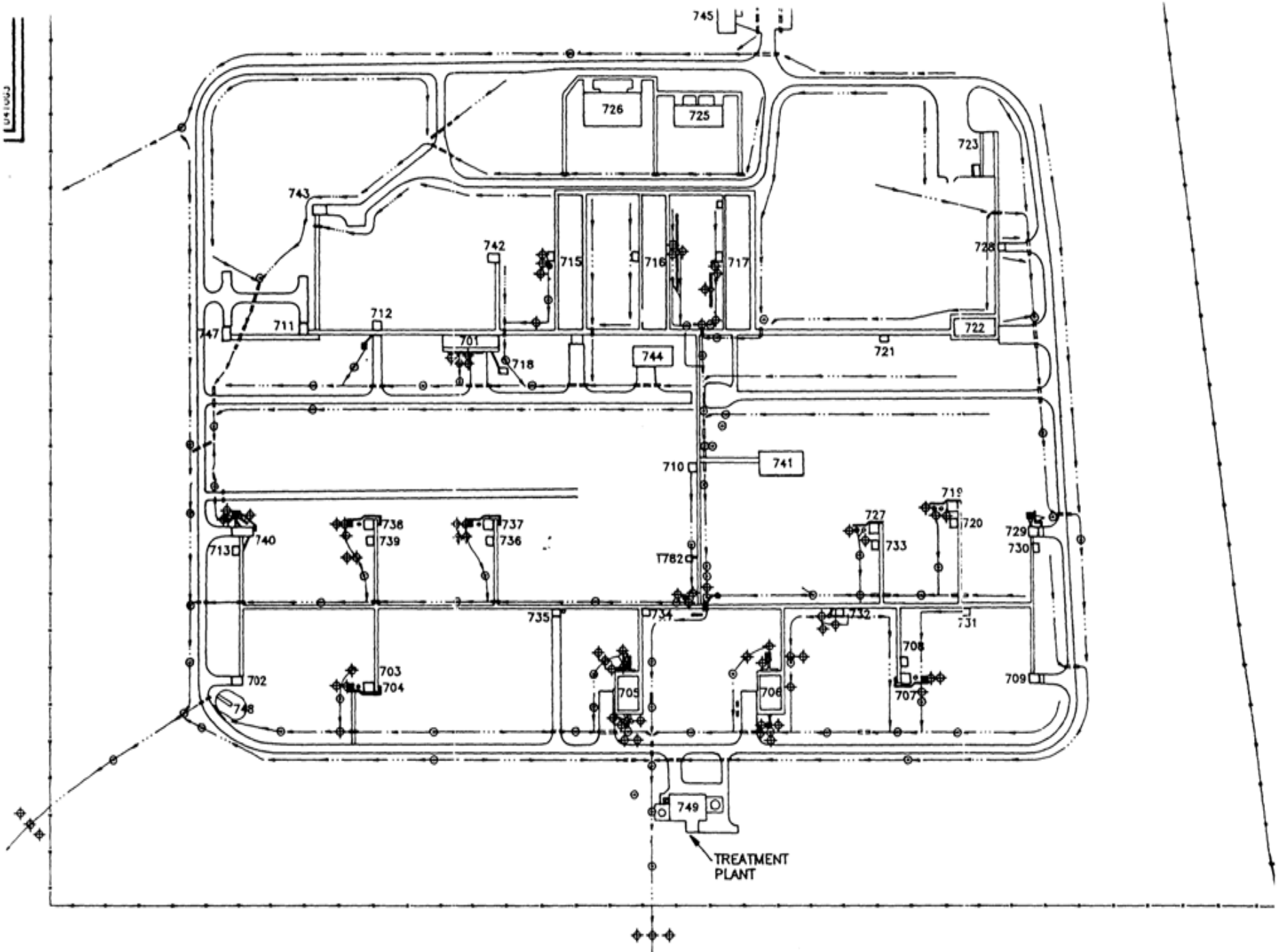


Figure 4-20. Point-detonating fuze.



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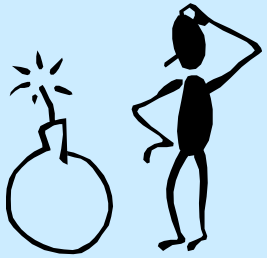
TREATMENT PLANT



700 AREA MANUFACTURING KSAAP

M55 Detonators

M219 Lead Cups

Boosters

Expulsion Charges

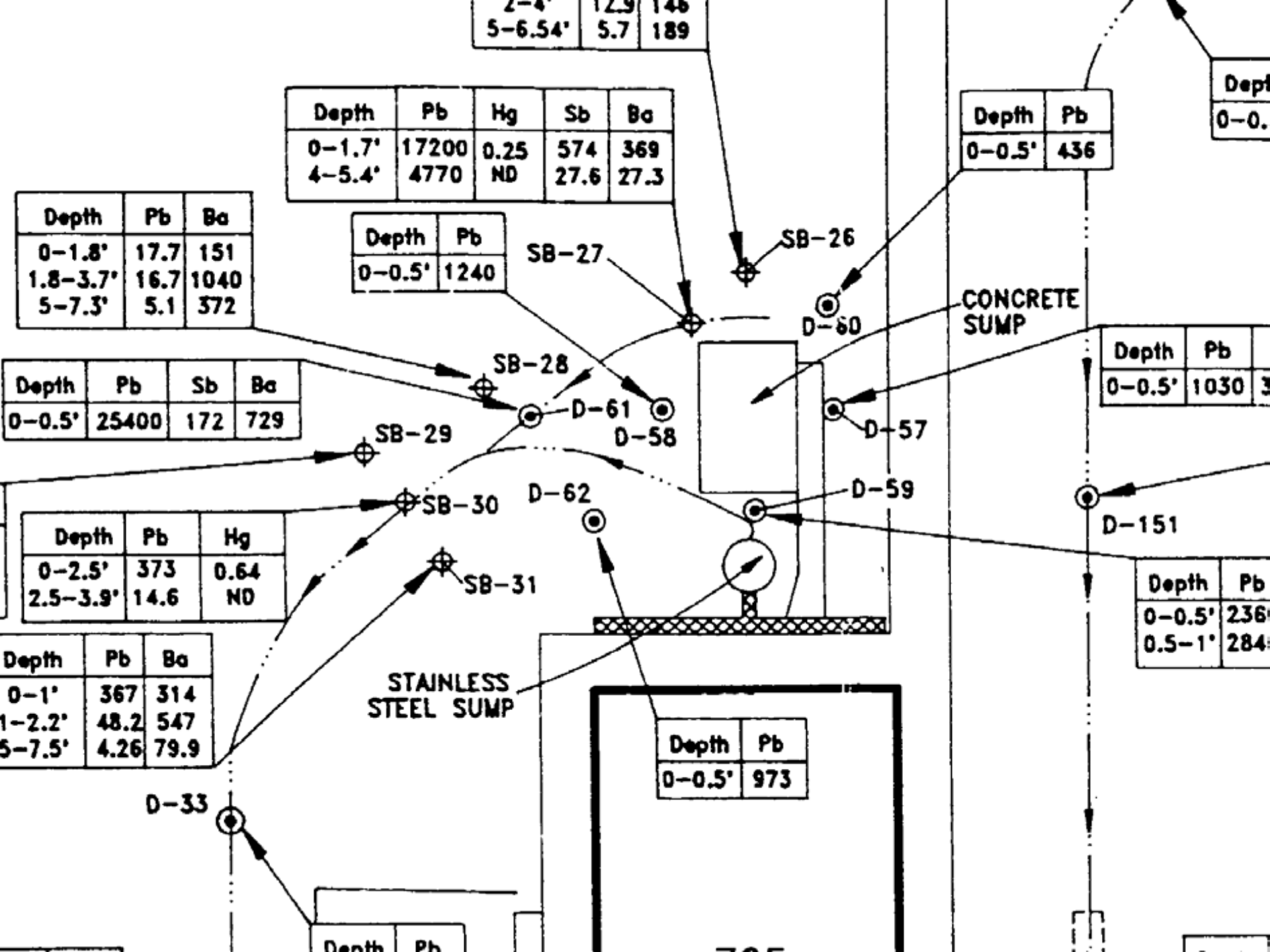
Bldg. 705 [Front]

Detonator Line, 700 Area

Moderate Lead Concentrations

Interim Removal Action

KSAAP 1998


2-4' 12.9 146
5-6.54' 5.7 189
Depth Pb Hg Sb Ba
0-1.7' 17200 0.25 574 369
4-5.4' 4770 ND 27.6 27.3
Depth Pb
0-0.5' 436
Depth Pb Ba
0-1.8' 17.7 151
1.8-3.7' 16.7 1040
5-7.3' 5.1 372
Depth Pb
0-0.5' 1240
SB-27
SB-26
D-60
CONCRETE SUMP
Depth Pb
0-0.5' 1030
SB-28
Depth Pb Sb Ba
0-0.5' 25400 172 729
D-61
D-58
D-57
SB-29
D-59
D-62
SB-30
D-151
Depth Pb Hg
0-2.5' 373 0.64
2.5-3.9' 14.6 ND
SB-31
Depth Pb
0-0.5' 236
0.5-1' 284
Depth Pb Ba
0-1' 367 314
1-2.2' 48.2 547
5-7.5' 4.26 79.9
STAINLESS STEEL SUMP
Depth Pb
0-0.5' 973
D-33

Bldg. 705 [Rear]

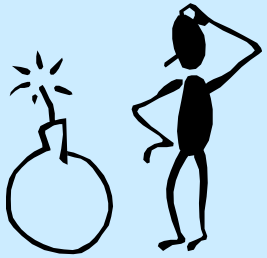
Detonator Line, 700 AREA

High Lead Concentrations

Interim Removal Action

KSAAP 1998

RVAAP INVESTIGATION



SOLUBILITIES METAL AZIDES

Lead Azide [$Pb(N_3)_2$]	**230 mg/L**	**@ 18 deg C**
Cupric Azide [$Cu(N_3)_2$]	**7 mg/L**	**“**
Sodium Azide [NaN_3]	**41,700 mg/L**	**“**
Potassium Azide [KN_3]	**49,600 mg/L**	**“**
Barium Azide [$Ba(N_3)_2$]	**16,700 mg/L**	**“**
Strontium Azide [$Sr(N_3)_2$]	**45,800 mg/L**	**“**

METHOD REACTIONS

EXTRACTION

$$M(N_3)_2 + 2\ NaOH \longrightarrow 2\ NaN_3 + M(OH)_2$$

M = Pb, Cu, Ca, Ba, Sr, etc.

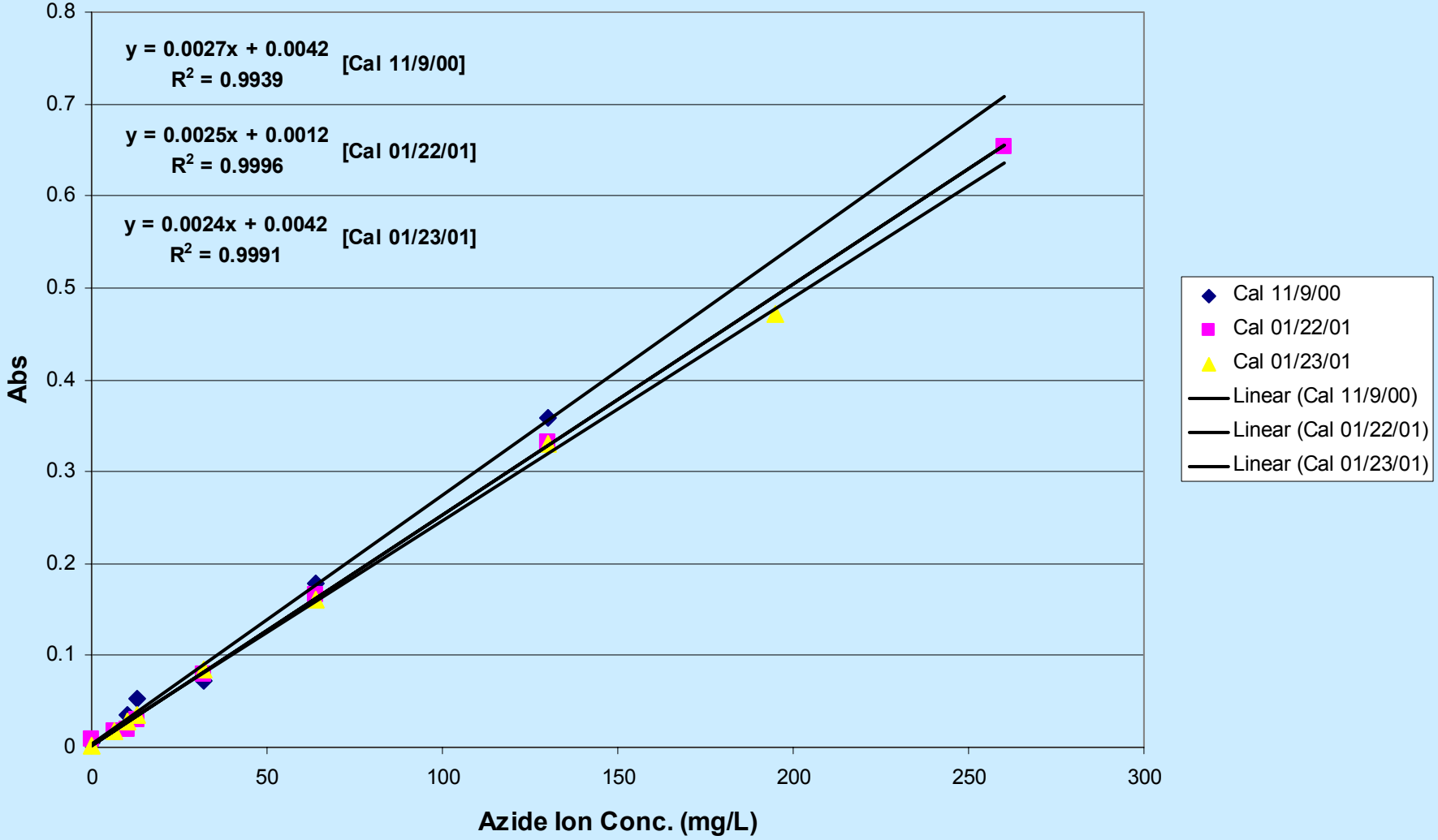
COLOR DEVELOPMENT

$$Fe(NO_3)_3 + 3\ NaN_3 \xrightarrow{H^+} Fe(N_3)_3 + 3\ NaNO_3$$

$$2\ Fe(NO_3)_3 + 3\ M(N_3)_2 \xrightarrow{H^+} 2\ Fe(N_3)_3 + 3\ M(NO_3)_2$$

AZIDE STANDARDS
RVAAP LL #9

AZIDE CALIBRATION CURVES

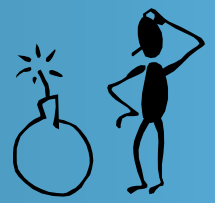


AZIDE INVESTIGATION RVAAP LL#9

Date:	Mar. 13, 2002					mg/Kg	
Sample No.	Type	Wt. Or Vol.	Dilution	Absorbance	Cal Factor	Concentration	% R
Blank				0.004			
50 ug Std				0.031	1612.90		
100 ug Std				0.057	1754.39		
250 ug Std				0.130	1923.08		
750 ug Std				0.378	1984.13		
1500 ug Std				0.766	1958.22		
Reagent Blank				0.004			
CCV1 (250)		1.00	1.00	0.129	1846.54	238.20	95%
CCV2 (750)		1.00	1.00	0.372	1846.54	686.91	92%
LL9SS-001-0001SO		5.00	5.00	0.030	1846.54	55.40	
LL9SS-001-0001SO-MS		5.00	5.00	0.082	1846.54	151.42	96%
LL9SS-001-0001SO-MSD		5.10	5.00	0.080	1846.54	144.83	90%
LL9SS-001-0001SO-DUP		5.00	5.00	0.037	1846.54	68.32	
LL9SS-002-0001SO		5.40	5.00	0.000	1846.54	63.26	
LL9SS-003-0001-SO		5.10	5.00	0.041	1846.54	74.22	
LL9SS-004-0001-SO		5.10	5.00	0.036	1846.54	65.17	
LL9SS-005-0001-SO		5.30	5.00	0.049	1846.54	85.36	
LL9SS-005-0001-SO-MS		5.30	5.00	0.094	1846.54	163.75	79%
LL9SS-005-0001-SO-MSD		5.20	5.00	0.085	1846.54	150.92	66%
LL9SS-006-0001-SO		5.00	5.00	0.023	1846.54	42.47	
LL9SS-007-0001-SO		5.40	5.00	0.028	1846.54	47.87	
LL9SS-008-0001-SO		5.00	5.00	0.022	1846.54	40.62	
LL9SS-009-0001-SO		5.20	5.00	0.022	1846.54	39.06	
LL9SS-010-0001-SO		5.40	5.00	0.024	1846.54	41.03	

AZIDE INVESTIGATION RVAAP LL#9 [Cont]

Sample No.	Type	Wt. Or Vol.	Dilution	Absorbance	Cal Factor	Concentration	% R
LL9SS-011-0001-SO		5.30	5.00	0.022	1846.54	38.32	
CCV3 (250)		1.00	1.00	0.130	1846.54	240.05	96%
LL6SS-001-0001-SO		5.00	5.00	0.021	1846.54	38.78	
LL6SS-002-0001-SO		5.20	5.00	0.040	1846.54	71.02	
LL6SS-003-0001-SO		5.40	5.00	0.044	1846.54	75.23	
LL6SS-004-0001-SO		4.80	5.00	0.027	1846.54	51.93	
LL10SS-001-0001-SO		5.00	5.00	0.023	1846.54	49.86	
LL10SS-002-0001-SO		5.00	5.00	0.027	1846.54	49.86	
LL10SS-003-0001-SO		5.20	5.00	0.026	1846.54	47.94	
LL9SS-001-0001-SO		1.00	1.00	0.026	1846.54	48.01	
LL9SS-001-0001-SO-AS		1.00	1.04	0.069	1846.54	132.51	85%
CCV4 (250)		1.00	1.00	0.128	1846.54	236.36	94%
LL9SS-001-0001-SO		1.00	1.00	0.032	1846.54	59.09	
LL9SS-001-0001-SO-AS		1.00	1.12	0.157	1846.54	324.70	89%
CCV5 (1500)		1.00	1.00	0.781	1846.54	1442.15	96%
DT34		5.10	5.00	0.032	1846.54	57.93	
DT34-MS		5.00	5.00	0.074	1846.54	136.64	79%
DT34-MSD		5.00	5.00	0.082	1846.54	151.42	93%
CCV6 (750)		1	1	0.392	1846.54	723.85	97%
Reagent Blank		1	1	0.009	1846.54	16.62	



PERCENT AZIDE SURFACE SOILS

Sample No.	Conc. Mg/Kg	% Azide Ion	% Lead Azide *
LL9SS-001-0001SO	55.40	0.006	0.008
LL9SS-001-0001SO-DUP	68.32	0.007	0.01
LL9SS-002-0001SO	63.26	0.006	0.008
LL9SS-003-0001-SO	74.22	0.007	0.01
LL9SS-004-0001-SO	65.17	0.007	0.01
LL9SS-005-0001-SO	85.36	0.009	0.12
LL9SS-006-0001-SO	42.47	0.004	0.006
LL9SS-007-0001-SO	47.87	0.005	0.007
LL9SS-008-0001-SO	40.62	0.004	0.006
LL9SS-009-0001-SO	39.06	0.004	0.006
LL9SS-010-0001-SO	41.03	0.004	0.006
LL9SS-011-0001-SO	38.32	0.004	0.006
LL6SS-001-0001-SO	38.78	0.004	0.006
LL6SS-002-0001-SO	71.02	0.007	0.01
LL6SS-003-0001-SO	75.23	0.008	0.011
LL6SS-004-0001-SO	51.93	0.005	0.007
LL10SS-001-0001-SO	49.86	0.005	0.007
LL10SS-002-0001-SO	49.86	0.005	0.007
LL10SS-003-0001-SO	47.94	0.005	0.007
LL9SS-001-0001-SO	48.01	0.005	0.007
LL9SS-001-0001-SO	59.09	0.006	0.008
DT34	57.93	0.006	0.008

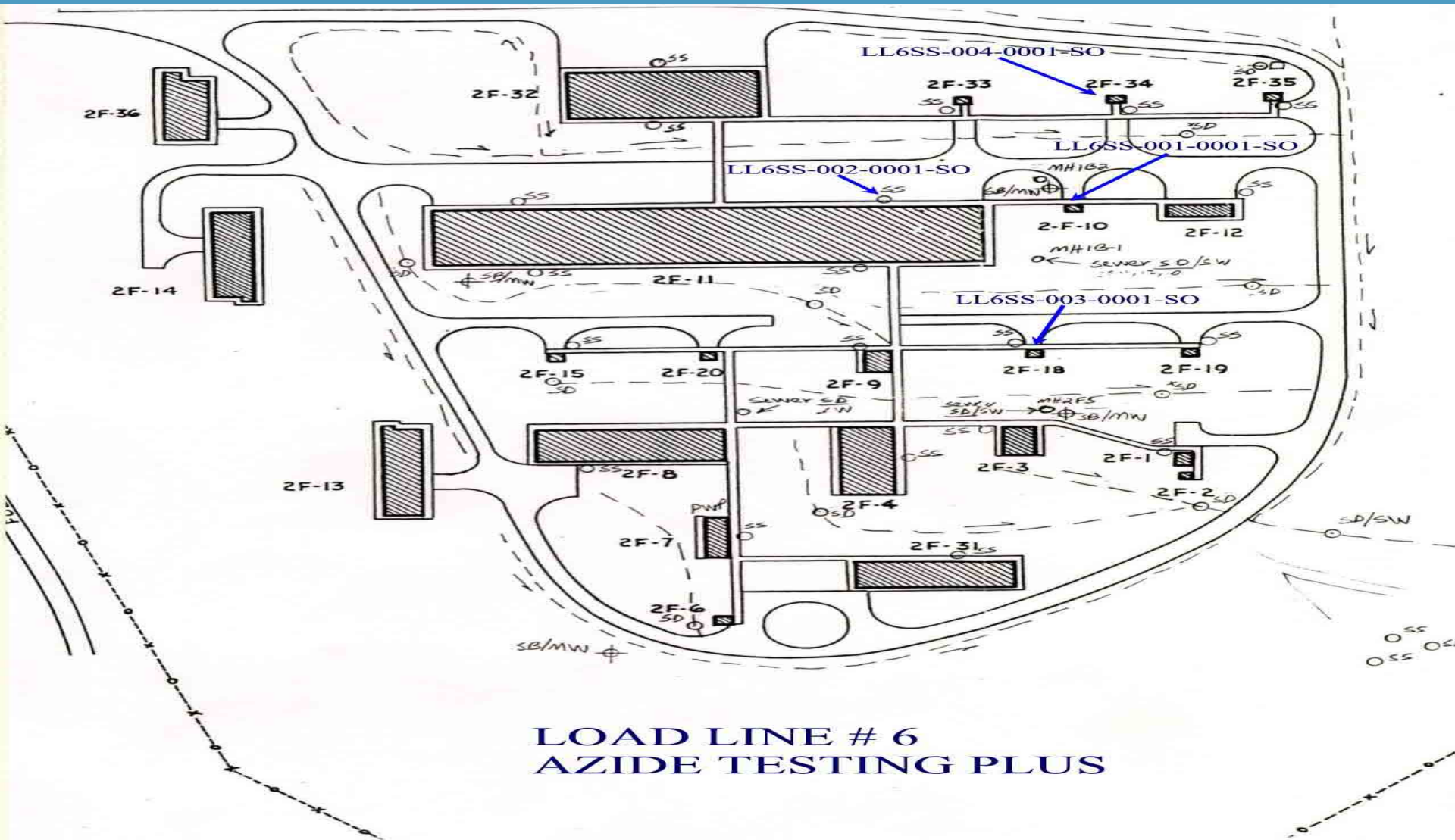
* Lead Azide Equivalent calculated from the Azide ion concentration

** Explosion Limit = 2.0% (20,000 Mg/Kg)

Building AP-7 Interior
Potential Lead Base Paint ----->
Concrete Dust----->
Concrete Dust----->
Concrete Dust

PROCESS ANALYSIS

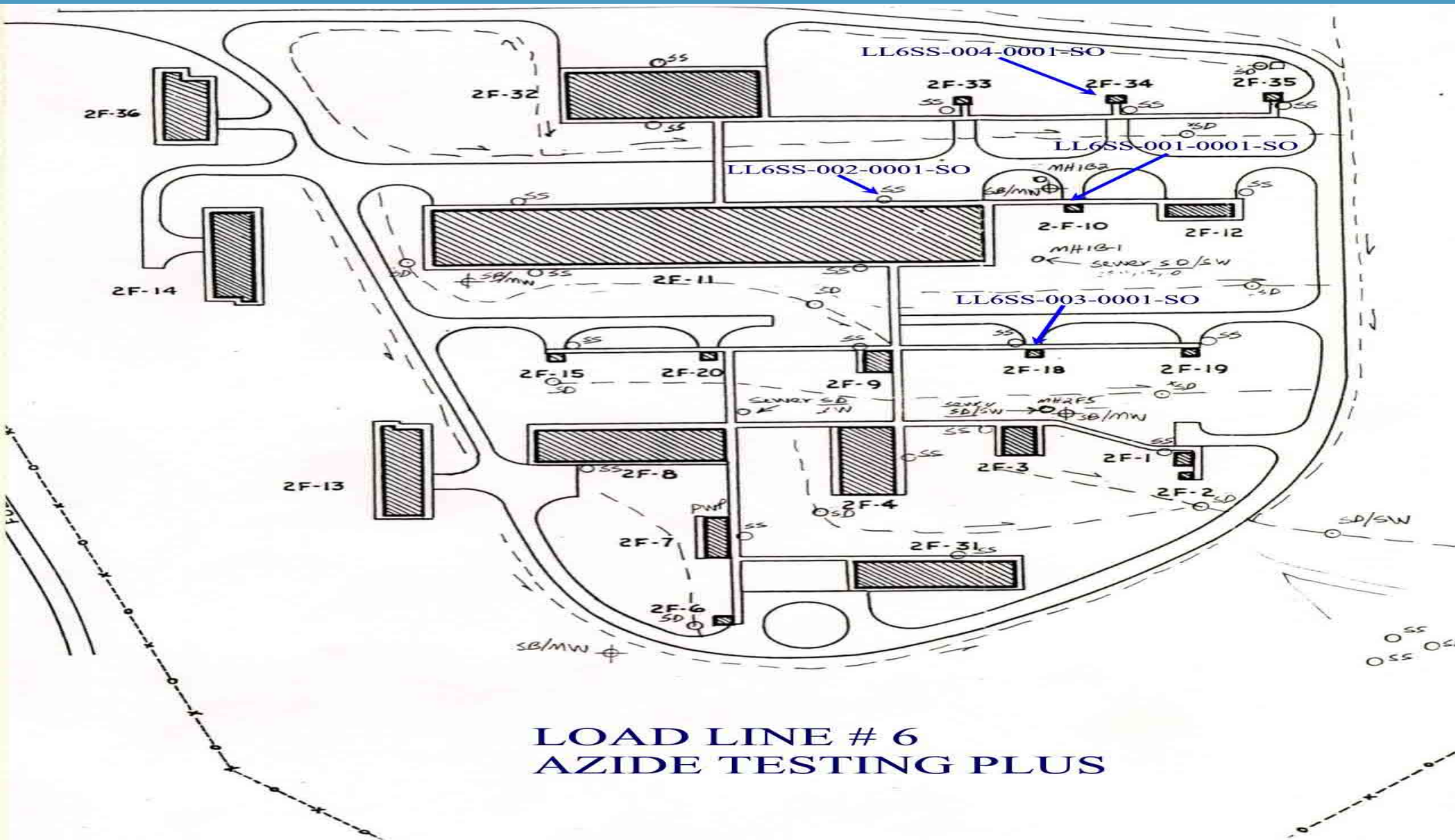
LOAD LINE #6
RVAAP



M106 MELT POUR MOD BLDG 2F-7

SHAPE CHARGE TESTING
BLDG # 2F-12 MOD

LOAD LINE #6
RVAAP



DRAGON FIRE TEST CHAMBER

TEST CHAMBER INTERIOR

MINE TEST POND

OPEN DETONATION AREA

PERCUSSION ELEMENT MFG LOAD LINE # 10

AOC Number **RVAAP-43**

NAME: Load Line 10 / Percussion Element

ASSOCIATED EXISTING AOC: RVAAP-26 (Fuse and Booster Area Settling Tanks)

REGULATORY PROGRAM: CERCLA

SIZE OF AOC: Nominal Fenced Area 1200-ft x 1400-ft; Approximately 39 acres

FUNCTION OF AOC: From 1941 – 1945 Load Line 10 operated at full capacity and produced 226,387,306 M-36 percussion elements. Load Line 7 was placed on standby in 1945.

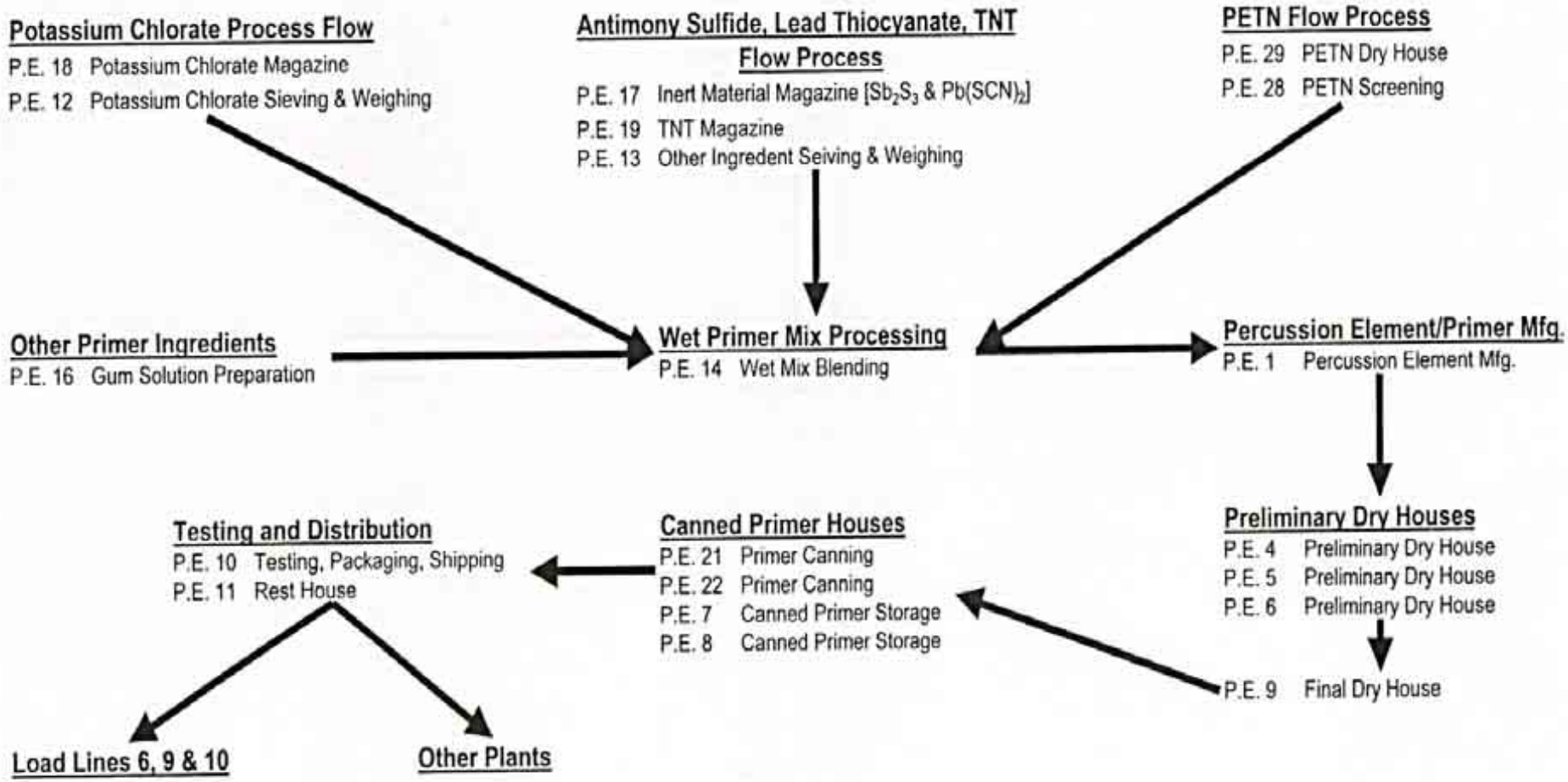
From 1951 - 1957, Load Line 10 produced the following items:

Primer, M36A1	21,716,950
Primer, M54	56,128,565
Primer, Perc, M61	43,912,850
Mfgr Metal Parts, F/Primer, M61	13,484,100
Perc Element	49,286,628

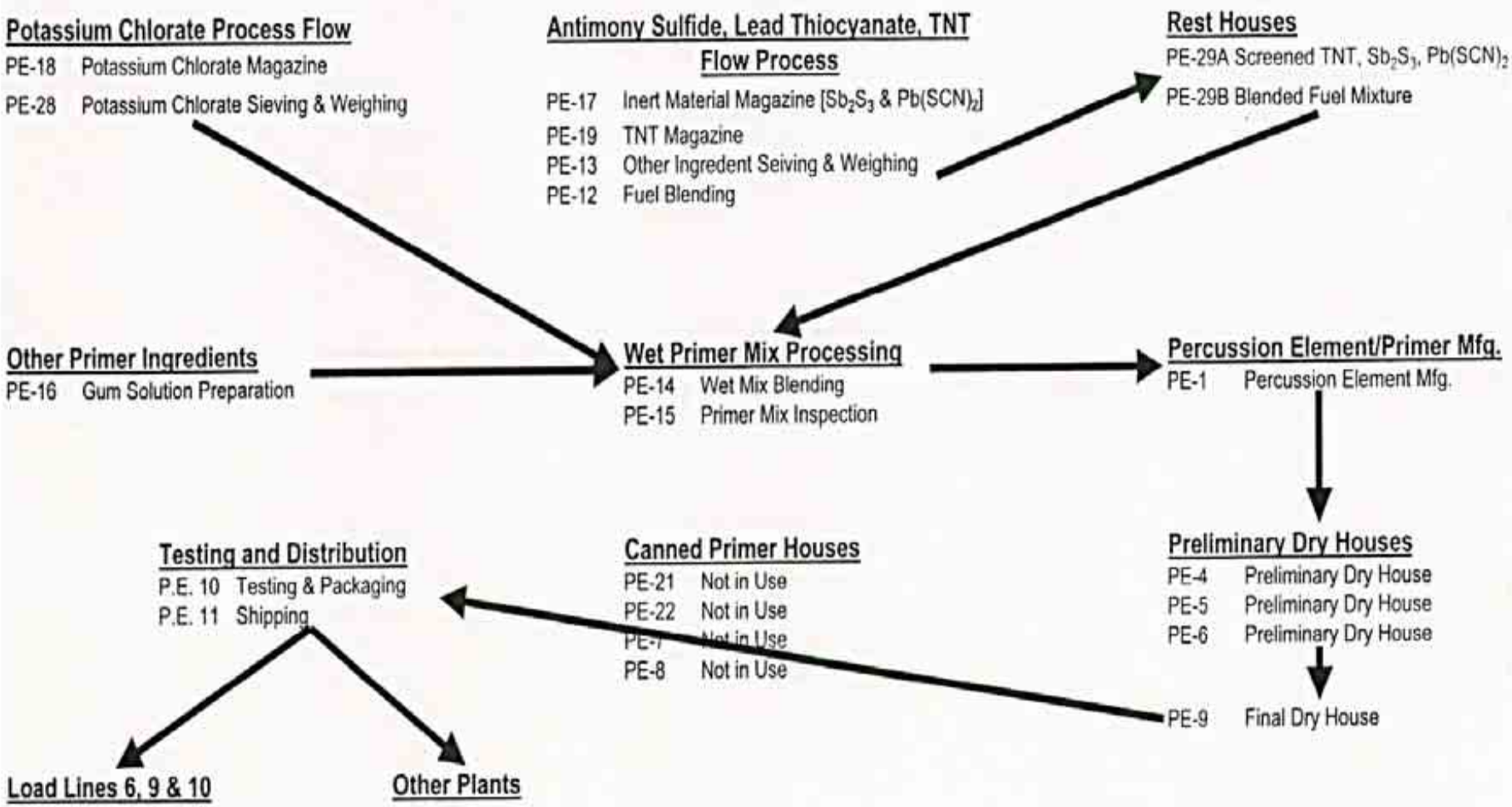
From 1969 - 1971, Load Line 10 produced 79,871,435 M54 Primers.

WASTE CHARACTERISTICS: Potential contaminants include lead azide, lead styphnate, black powder, TNT, Composition B, **antimony sulfide, lead thiocyanate,** explosives, propellants, and TAL metals. Contamination is potentially present on the facilities interior surfaces, in exterior soils, and in the holding tanks and settling ponds which comprised the wastewater treatment system. Additionally the storm sewer and surface water discharge points are potentially contaminated as well.

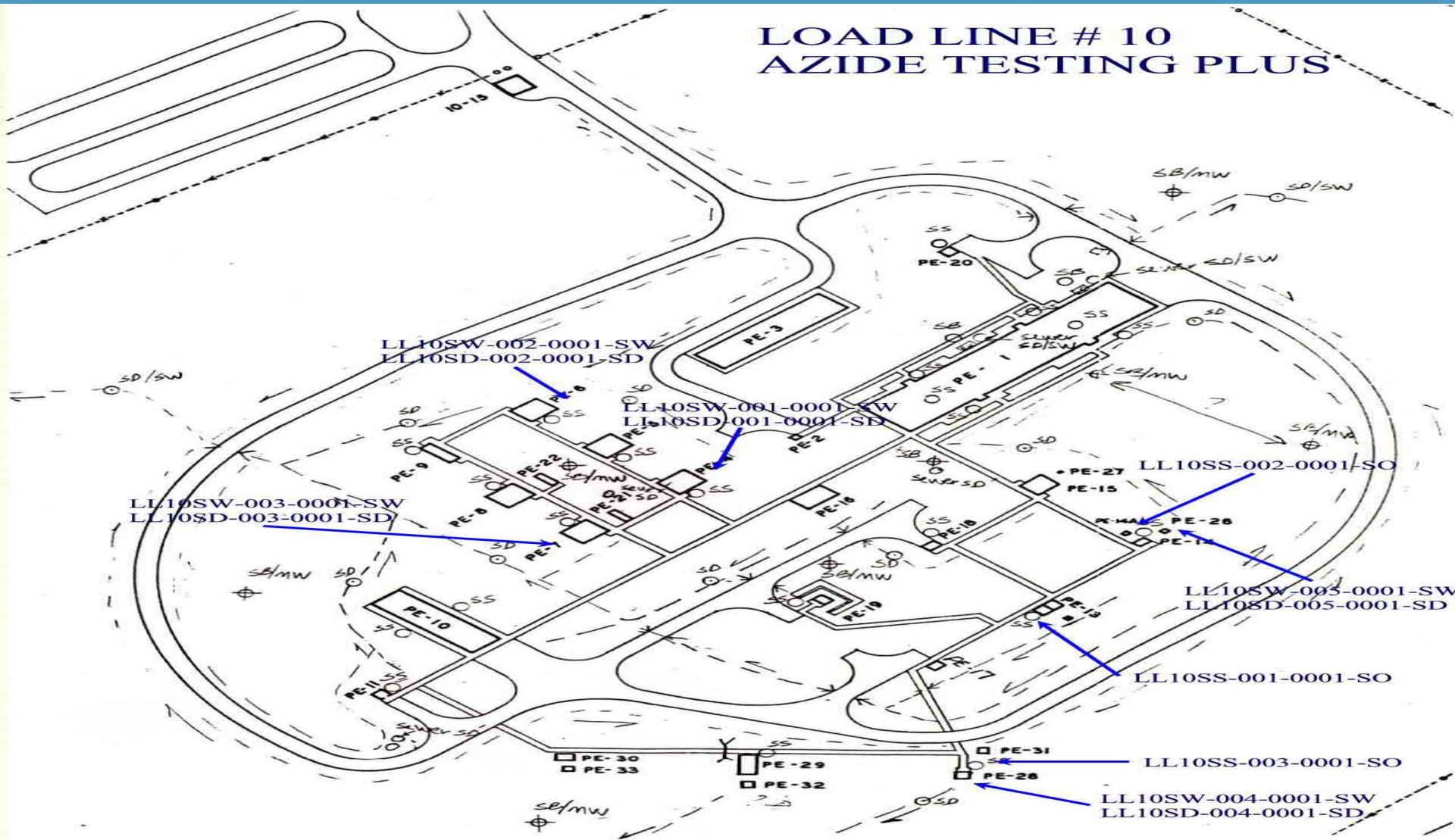
RAVENNA ARMY AMMUNITION PLANT
Load Line # 10 [Percussion Element Primers]
[1956 Production Scheme]



RAVENNA ARMY AMMUNITION PLANT
Load Line #10 [Percussion Elements/Primers]
[1969-1971 M-54 Primer Production Scheme]

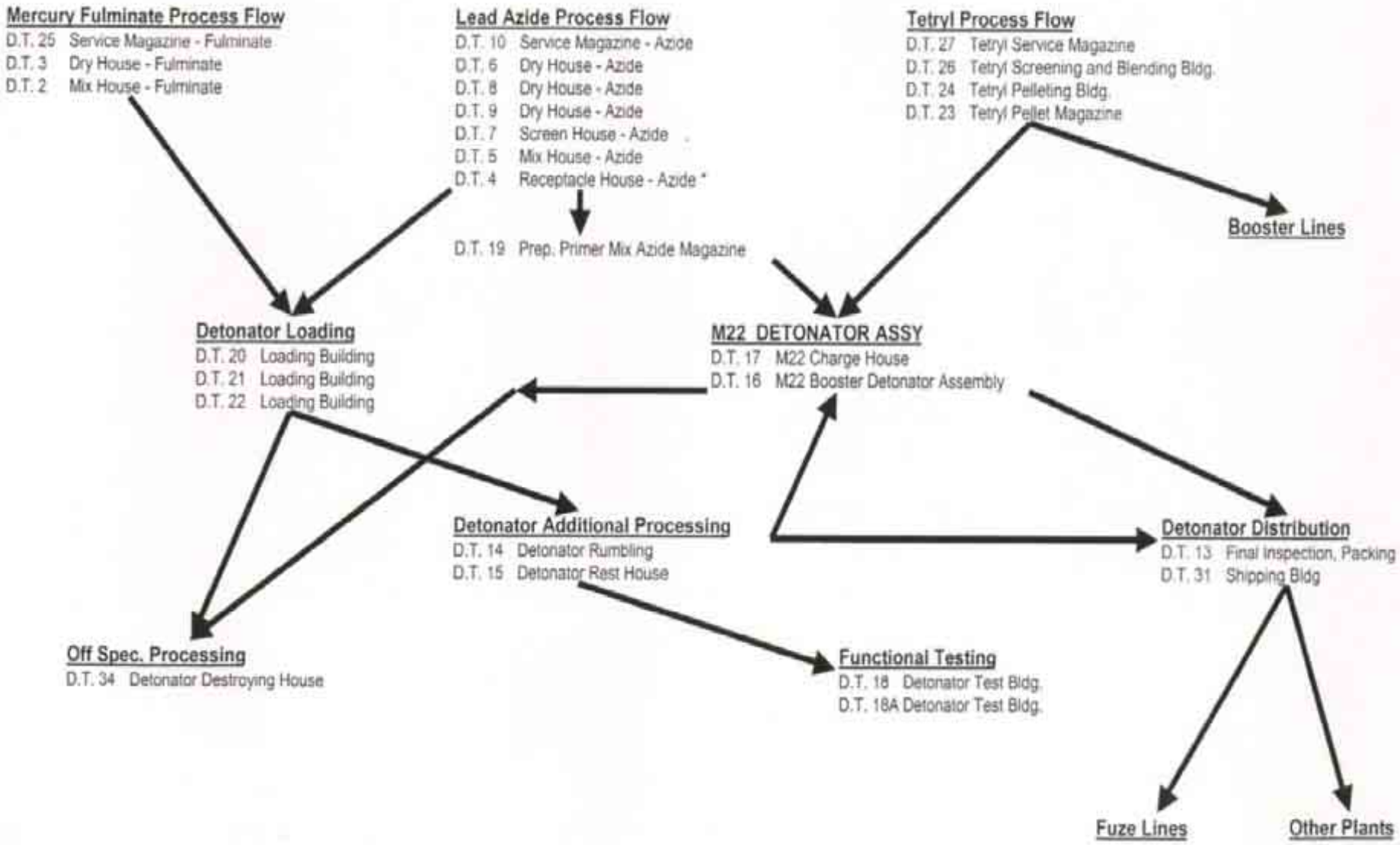


LOAD LINE # 10
RVAAP



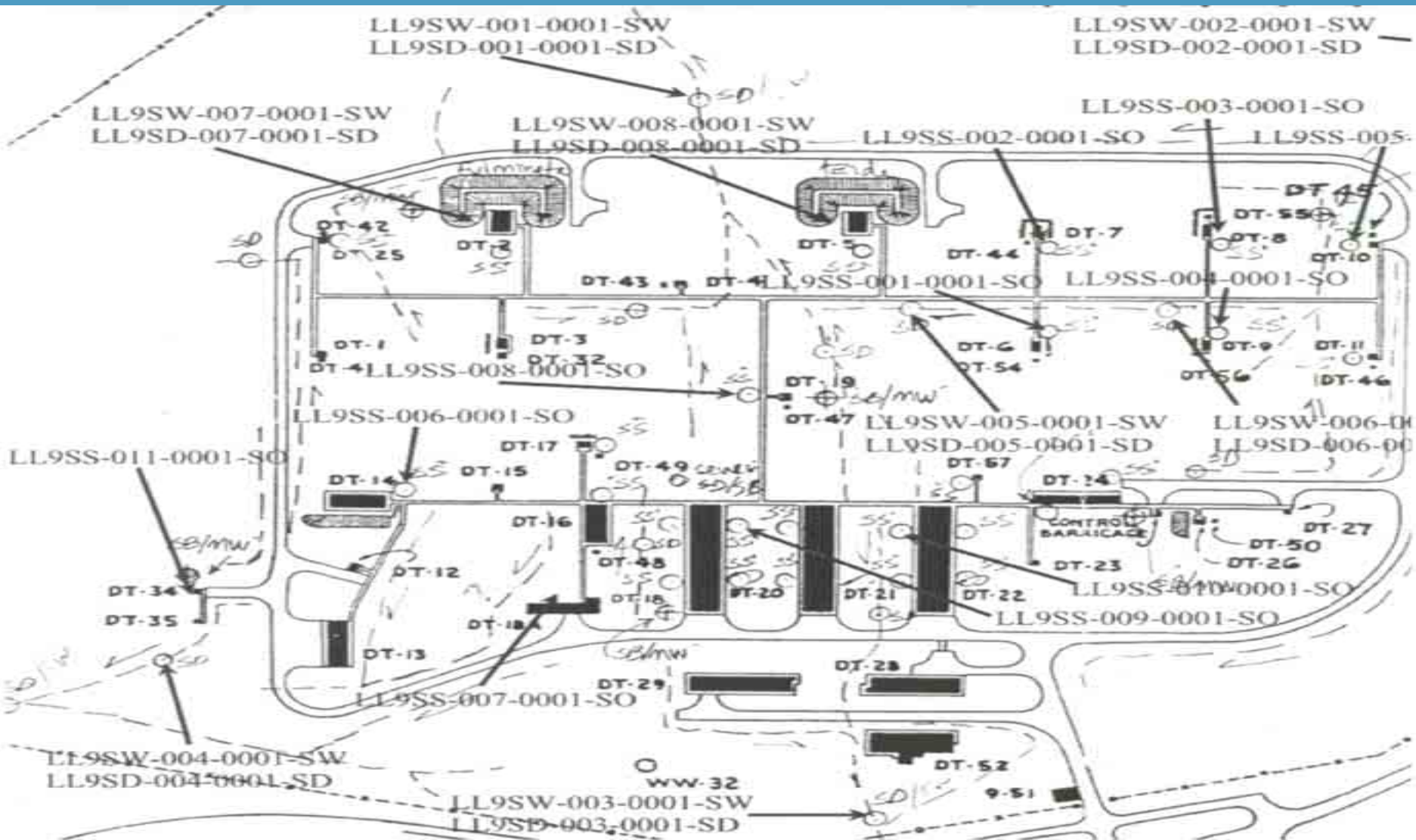
RAVENNA ARMY AMMUNITION PLANT

Load Line #9 [Detonator Manufacturing

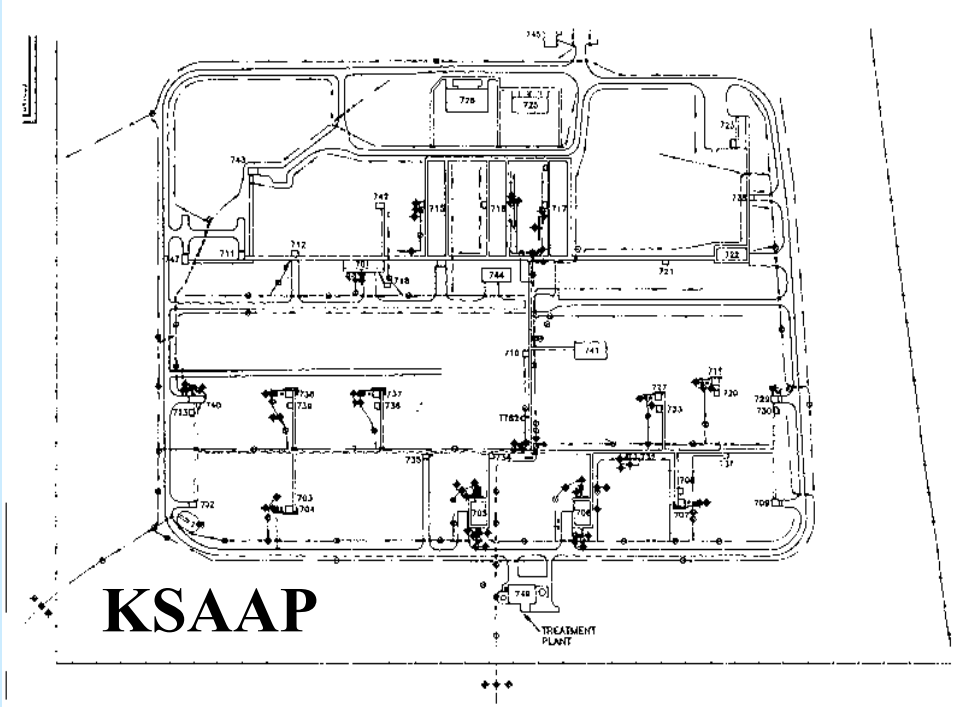


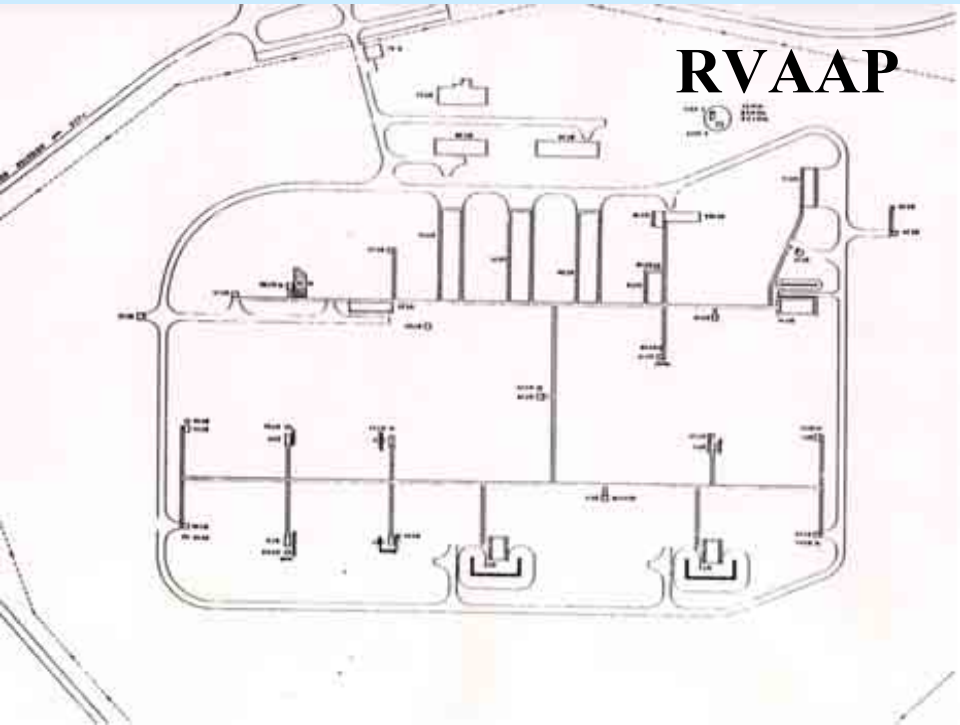
* Receptacle is comparable to a Rest House

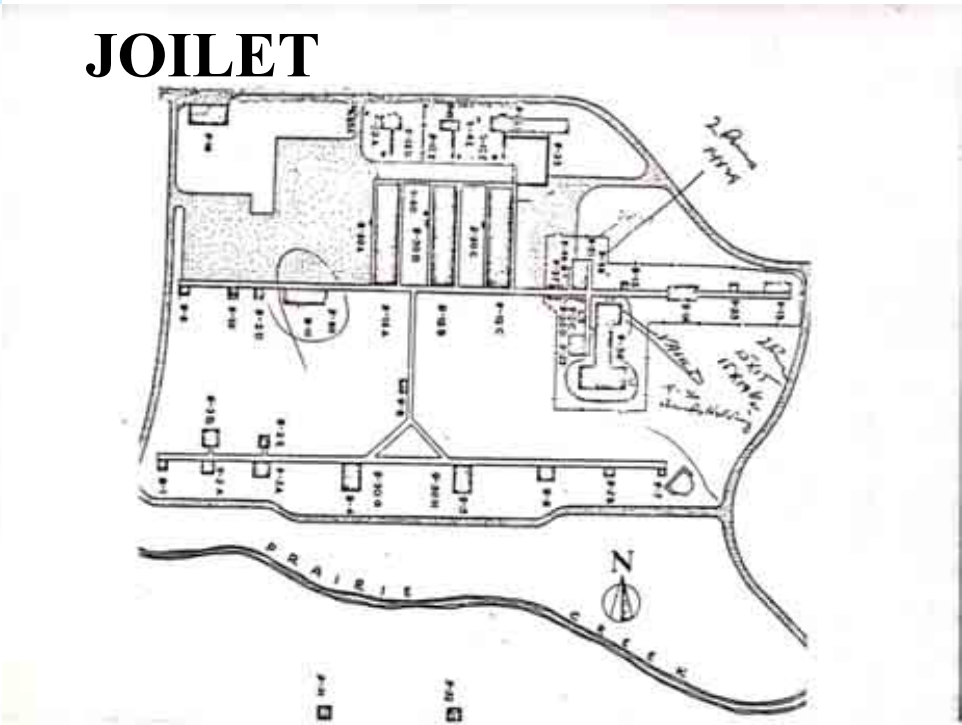
LOAD LINE #9
RVAAP



Detonator Manufacturing Lines



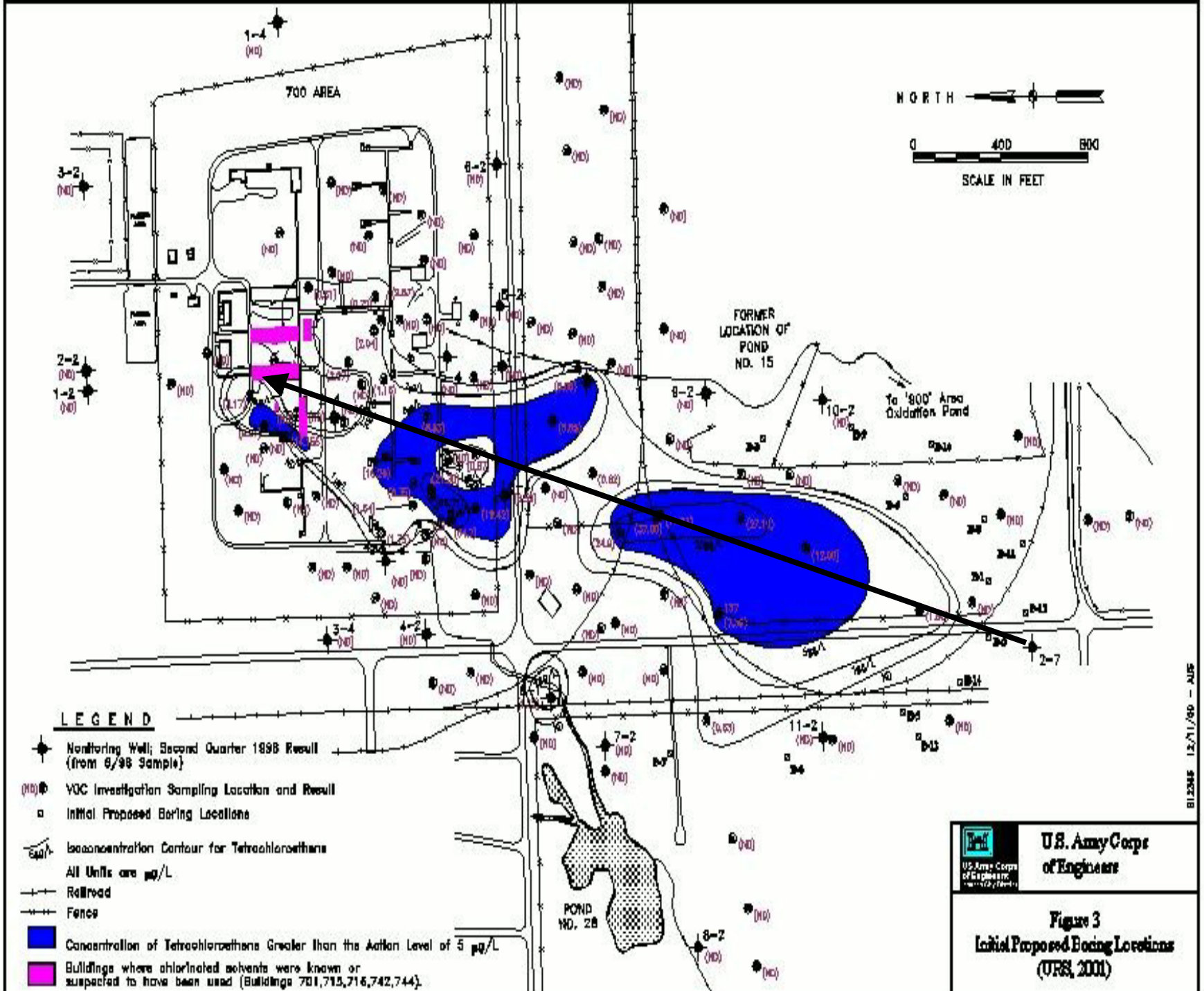




Loader [Detonators & Lead Cups]

LOAD LINE # 9
DETONATOR MANUFACTURING

Booster Loader [Tetryl & RDX]


700 AREA
NORTH
0 400 800
SCALE IN FEET
FORMER LOCATION OF POND NO. 15
To '800' Area Oxidation Pond
POND NO. 28
LEGEND
Monitoring Well; Second Quarter 1998 Result (from 6/98 Sample)
VOC Investigation Sampling Location and Result
Initial Proposed Boring Locations
Isoconcentration Contour for Tetrachloroethene
All Units are µg/L
Railroad
Fence
Concentration of Tetrachloroethene Greater than the Action Level of 5 µg/L
Buildings where chlorinated solvents were known or suspected to have been used (Buildings 701,715,716,742,744).
U.S. Army Corps of Engineers
Figure 3
Initial Proposed Boring Locations
(URS, 2001)

Common Deactivation Processes

Lead Azide Process

- > $NaNO_2/CH_3COOH$
- > $Ce(NH_4)_x(NO_3)_y$ or $Ce(SO_4)_2$
- > NaOH

Lead Styphnate Process

NaOH/Al (Cold & Hot)

$NaCO_3$/Steam/Al

RDX Process

NaOH/Steam

AREAS OF APPLICATION

Trinitroresorcinol Manufacturing

Lead Styphnate Manufacturing

Primer Mix Manufacturing

Primer Assembly

Lead Azide Deactivation Process

Method I

$$Na\,NO_{2\,(aq)} + CH_3COOH \text{ ----------> } HNO_{2(aq)} + Na^{+} + CH_3COO^{-}$$

a). $Pb(N_3)_{2(aq)} + 2HNO_{2(aq)}$ -----> $Pb^{+2}{}_{(aq)} + 2N_{2(g)} + 3\,N_2O_{(g)} + H_2O$

b). $Pb(N_3)_{2(aq)} + XsHNO_{2(aq)}$ --------> $PbO\,H_2O_{(aq)} + 4N_{2(g)}$

Method II

$$Pb(N_3)_2 + 2Ce(SO_4)_2 \text{ ---------> } PbSO_4 + Ce_2(SO_4)_3 + 3N_2$$

Lead Azide Deactivation Process

METHOD USED FOR AZIDE DEACTIVATION

[Prior to Drilling in 700 Area]

$$Pb(N_3)_{2\,(s)} + 2\,NaOH_{(aq)} \text{----------}> 2\,NaN_{3\,(aq)} + PbO \cdot H_2O$$

NATURAL ATTENUATION

NaN_3 + (Moistened Soil) + Micro-organisms -----> Nitrogen Nutrients

Reference: US Patent 3,376,125

Application Rate 0.5 to 500 Lbs/Acre

Half Life of Azide Residual = 3 to 13 days

Maximum Life Observed = 30 days

Lead Styphnate Deactivation Process

$$C_6H(NO_2)_3O_2Pb{\cdot}H_2O + 2NaOH \text{ ------> } PbO{\cdot}H_2O + C_6H(NO_2)_3O_2^{-2} + 2Na^+$$

Lead Styphnate — Sodium Hydroxide — Lead Hydroxide — Trinitroresorcinol Ion

$$2NaOH + Al \text{ ----------> } NaAlO_2 + H_2 + Na^+$$

Ideal Reaction

$$C_6H(NO_2)_3O_2^{-2} + 4H_2 \text{ ---------> } C_6H(NH_2)_3(OH)_2$$

Trinitroresorcinol Ion — Triaminoresorcinol

Actual Reaction Products Include:

Nitrosoamines, Hydroxyl Amines, Azoxy & Azo Compounds

Lead Styphnate Deactivation Process

$$C_6H(NO_2)_3O_2Pb{\cdot}H_2O + 2Na_2CO_3 \xrightarrow{\text{Steam}} PbO{\cdot}H_2O + C_6H(NO_2)_3O_2^{-2} + 2Na^+$$

$$Na_2CO_3 + H_2O \xrightarrow{\text{Steam}} NaOH + CO_2$$

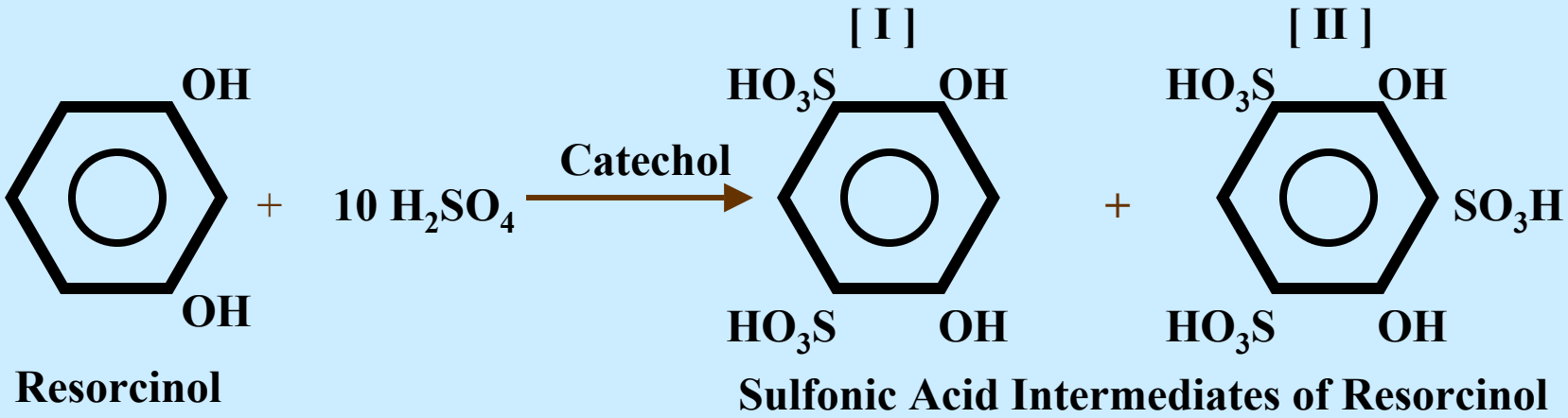
$$2NaOH + Al \longrightarrow NaAlO_2 + H_2 + Na^+$$

<u>Yields Similar Products</u>

$$C_6H(NO_2)_3O_2^{-2} + 4H_2 \longrightarrow C_6H(NH_2)_3(OH)_2$$

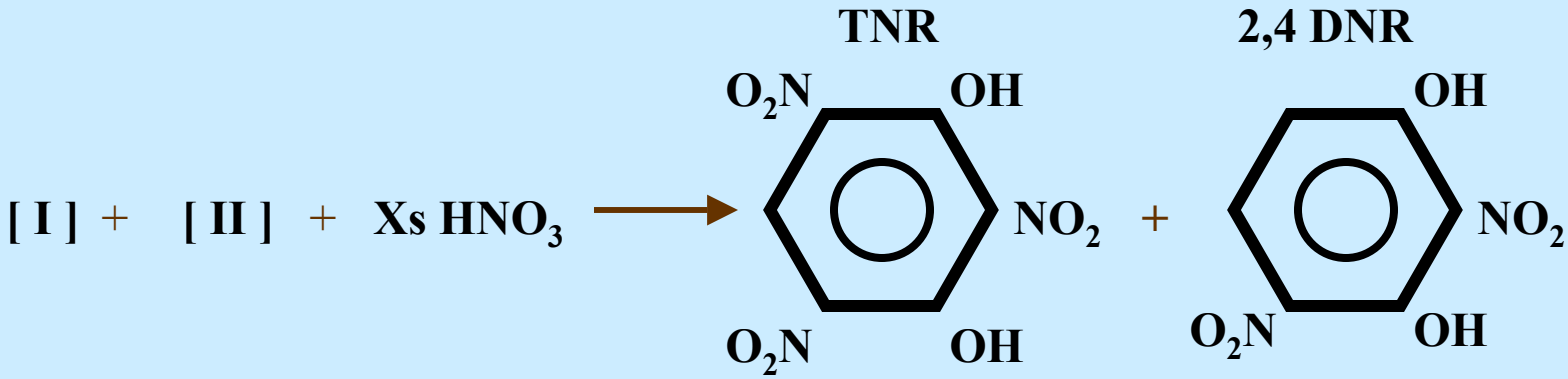
Nitrosoamines, Hydroxyl Amines, Azoxy & Azo Compounds

TNR SYNTHESIS LCAAP

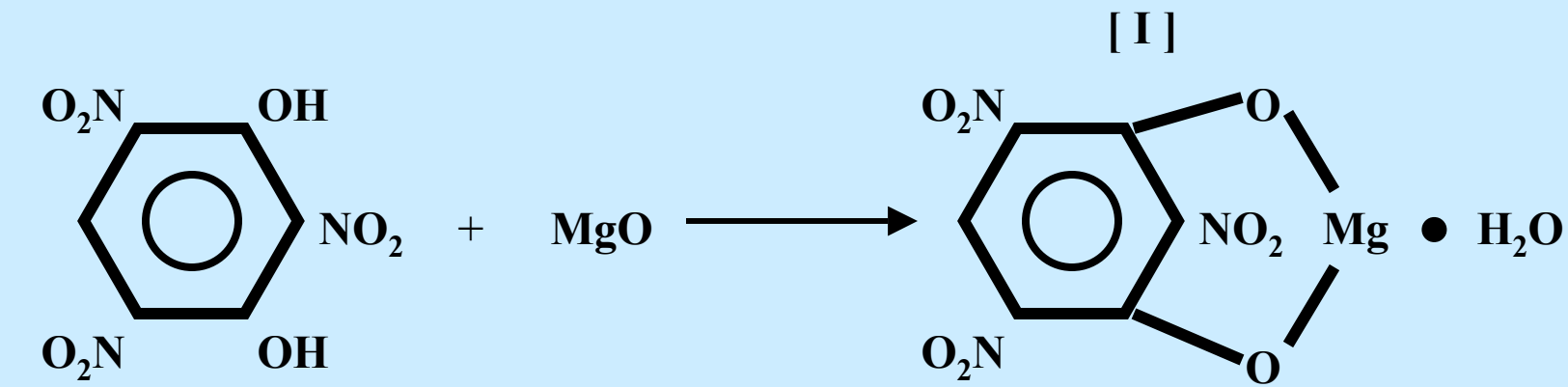


Resorcinol

Sulfonic Acid Intermediates of Resorcinol

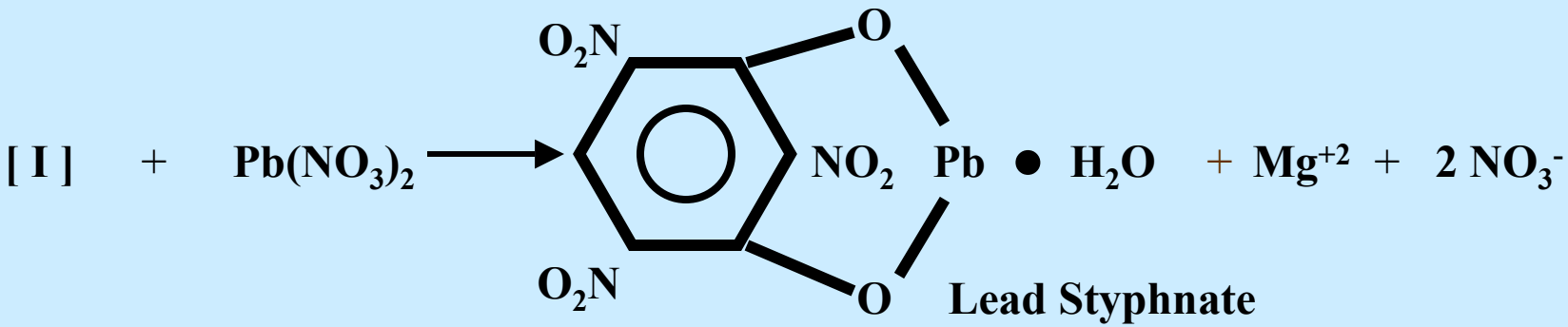


LEAD STYPHNATE SYNTHESIS



Trinitroresorcinol

Magnesium Styphnate



Lead Styphnate