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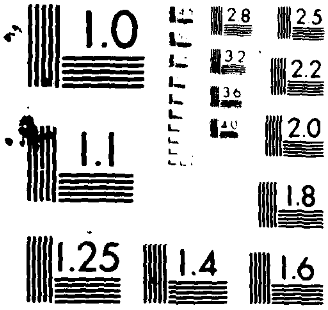

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report describes laboratory studies of the purification of crude 2,4,6-trinitrotoluene (TNT) using ammonium sulfite and magnesium sulfite hexahydrate. The magnesium sulfite hexahydrate purification process produces acceptable TNT, but the TNT produced using ammonium sulfite has low set points.

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20. ABSTRACT (cont)

From laboratory studies, the red water resulting from the purification of TNT using magnesium sulfite hexahydrate can be easily concentrated and the magnesium sulfite hexahydrate recovered for recyling into the TNT purification system.

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INTRODUCTION

Trinitrotoluene (TNT) must be purified before it can be of value as an explosive. Crude TNT is composed of α-TNT and unsymmetrical TNT isomers. For years the Sellite process (where TNT is contacted with sodium sulfite) has been employed for purifying TNT. The purification process removes the unsymmetrical TNT isomers by converting them into water soluble dinitrotoluene sulfonates. The aqueous wash solution from the Sellite process is commonly referred to as red water and also contains complexed α-TNT and various oxidation products.

The customary red water treatment approach is the incineration of a concentrated solution of the red water in a rotary kiln to produce an ash. The ash creates several problems. When landfilled, the ash will produce a leachate which may contain nitroaromatics. Although the ash has been landfilled with plastic liners, a leachate still may be produced and create a problem with time. Red water was once sold to paper mills for its sodium and sulfur values but the Environmental Protection Agency has now classified red water as a hazardous waste material. Because of this ruling, paper mills refuse to accept red water due to severe transportation and plant operational restrictions.

Efforts have been directed toward developing a pollution free TNT purification and waste disposal process. Candidates were: (1) Sellite process with sulfite recovery via the Sonoco process, (2) magnesium sulfite purification and disposal process, (3) the nitric acid recrystallization process and (4), ammonium sulfite purification. The first three processes were evaluated and reported in June 1979 under, "Task I - Comparative Cost Study of Purification Methods," Production Engineering Report 556. The ammonium sulfite purification process was evaluated in and reported in the March 1976 PE-503 report entitled, "Ammonium Sulfite Purification of TNT." A cost study for utilization of ammonium sulfite in the purification of TNT was reported in September 1980 under, "Task II - Comparative Cost Study of Purification Methods."

Also, additional laboratory evaluations of the ammonium sulfite purification process are presented. This report describes the magnesium sulfite purification process and provides data on the laboratory purification runs.

STUDY

Ammonium Sulfite Purification

Previous studies under PE-503 have shown that set point depression occurs with ammonium sulfite ($(NH_4)_2SO_3$) purified TNT because of the presence of meta-amino-dinitrotoluenes (amino-DNT) from the unsymmetrical isomers. In order to determine if amino compounds are also produced from 2,4,6-TNT, a sample of high purity TNT from the batch TNT process with a set point of 80.63°C was treated with $(NH_4)_2SO_3$ solution in a 4:1 mole ratio. The reaction vessel was a 1000 mL resin flask equipped with a four hole cover and was positioned in a large beaker of boiling water mounted on a magnetic stirrer hot plate. A thermometer and pH probe were inserted in two of the holes of the cover. Approximately 90-100g of molten TNT was poured into the tared reaction vessel to obtain an exact weight of TNT. The reaction flask was then placed in the boiling water and after the TNT melted, 300 mL of boiling water was added and the magnetic stirrer turned on.

The purification solution was prepared from an ammonium bisulfite solution which was adjusted to pH 7.5 with ammonium hydroxide. The set point measurement for the $(NH_4)_2SO_3$ treated TNT was 80.75°C and represents an improvement, presumably caused by the removal of the final 0.09 percent meta isomers which was present in the high purity TNT. Thin layer chromotographic (TLC) analysis of the product showed no amino-DNT formation or any other anomalous compound. This indicates that the by-product formation reactions of $(NH_4)_2SO_3$ are only associated with the meta TNT isomers.

A series of $(NH_4)_2SO_3$ purification runs were conducted on crude TNT obtained from the Volunteer Army Ammunition Plant (VAAP) acid washer. Data from these runs are shown in table 1. Generally, set points were low and appeared to be related to the amino-DNT content. The meta-TNT isomer removal was essentially complete except for Runs No. 27, 28 and 29.

Three variations were made in the laboratory purification process to reduce the amino-DNT level and improve the TNT set point. The variations were, incremental addition of the $(NH_4)_2SO_3$, reduction of pH and a combination of the two. The first two runs were made without pH control and all the $(NH_4)_2SO_3$ was added at one time. Runs No. 3 through 7 were made without pH control and incremental addition of the $(NH_4)_2SO_3$. Runs No. 27 through 29 were made with pH control using a weak sulfuric acid (H_2SO_4) solution and all $(NH_4)_2SO_3$ being added at one time. Runs No. 30 through 39 were made with pH control and incremental addition of the $(NH_4)_2SO_3$.

Table 1. Summary of TNT purification using ammonium sulfite

Run no.	Mole ratio TNT $(NH_4)_2SO_3$	Set Point °C	pH reactor	Total vol of water mL	Temp of reactor °C	Product Analysis				
						3-Amino 2,4-DNT	5-Amino 2,4-DNT	DNT	TNT 2,4,6	TNT meta
1*	3.88:1	78.80	8.4	100	---	0.06	0.02	0.10	97.58	2.31
2*	4.05:1	78.70	8.7	100	---	0.15	0.13	0.11	97.70	2.01
3	4.05:1	79.00	9.3	100	---	0.91	0.90	0.10	99.00	ND
4	4.08:1	79.80	9.5	100	---	0.85	0.80	0.10	99.52	0.02
5	4.10:1	79.36	9.6	100	---	0.56	0.47	0.10	99.37	0.07
6	4.00:1	78.92	8.7	100	---	0.57	0.58	0.10	98.72	0.62
7	4.00:1	78.90	9.0	100	---	0.80	1.00	0.10	98.84	0.06
27*	4.1:1	78.7	7.5	100	80	0.20	0.15	0.07	97.45	2.33
28*	4.16:1	78.7	7.0	100	80	0.31	ND	0.05	97.49	2.45
29*	4.1:1	78.50	7.0	100	80	0.09	0.01	0.06	96.96	2.98
30	4.1:1	79.43	7.3	100	84	0.36	0.40	0.06	99.49	0.05
31	4.1:1	79.60	7.7	100	85	0.36	0.28	0.06	99.63	0.03
32	4.1:1	79.76	7.7	100	88	0.30	0.25	0.06	99.67	ND
33	4.1:1	79.20	7.6	100	92	0.78	0.60	0.07	99.34	ND
34	4.1:1	80.22	7.2	100	85	0.25	0.10	0.06	99.84	ND
35	4.1:1	79.95	7.7	100	88	0.17	0.22	0.06	99.72	ND
36	4.1:1	79.58	7.2	100	85	0.12	0.06	0.06	99.40	0.48
37	4.1:1	79.90	7.6	100	85	0.33	0.27	0.06	99.67	ND
38	4.1:1	79.87	7.2	100	85	0.22	0.13	0.06	99.81	ND
39	4.1:1	79.97	7.4	100	85	0.24	0.16	0.06	99.77	ND

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*All $(NH_4)_2SO_3$ added at one time

Although these data did not reflect acceptable set point material, TNT purified under batch process conditions (PE-503) was acceptable. In these studies, the TNT was molten. Under these conditions the ammonium ion is more effective in the substitution reaction to form amino-DNT's.

Purification by Direct Addition of Magnesium Sulfite Hexahydrate

The first phase of the $MgSO_3$ study consisted of adding solid $MgSO_3$ directly to the reaction vessel and varying the TNT to $MgSO_3$ mole ratio. The addition of $MgSO_3$ was accomplished by adding the entire amount, based on the moles of TNT, in one increment and allowing it to react for 15 minutes or adding it in small increments over a period of 15 minutes. At the end of the purification cycle the stirrer was turned off to allow the water and molten TNT phases to separate. Phase separation was very difficult due to a very stable emulsion. A reduction in pH from 8-9 to 3-4 at the end of the purification cycle allowed the two phases to rapidly separate without any effect on the purity of the TNT.

Direct addition was used for Runs No. G-8 through G-13 and incremental addition was used for Runs No. G-14 and G-26 and G-40 through G-43 (see **table** 2). Runs No. G-11 and G-13 were made with the pH adjusted to 7.5 using SO_2 and No. G-8 through G-10 were conducted without pH adjustment. The pH was adjusted to determine if the lower pH would increase the meta-TNT removal efficiency, but the opposite was found. The incremental addition of solid $MgSO_3$, which has a low water solubility, was adopted to alleviate the settling of the $MgSO_3$ in the reaction vessel.

A summary of the effect of mole ratio of TNT to $MgSO_3$ on set point of the purified TNT is shown in **figure** 1. The data indicate that the mole ratio should be between 4 and 12 to achieve an acceptable product.

Purification by Recyling Magnesium Sulfite

The direct addition of $MgSO_3$ indicated that TNT could be purified with set points well above the minimum value of 80.20°C. In plant operation, the $MgSO_3$ solid salt could not be added directly to the purification vessels. The undissolved salt could possibly be retained in the molten TNT after it leaves the separator and contaminate the purified product. Also, in the continuous process, not enough $MgSO_3$ will dissolve in the aqueous phase to remove all of the unsymmetrical TNT isomers. To alleviate the difficulty of adding $MgSO_3$, a recycle process was investigated.

Table 2. Summary of TNT purification using magnesium sulfite

Run no.	Mole ratio TNT to MgSO$_3$	Set point °C	pH reactor	%MgSO$_4$ added	Total vol. of water L	MgSO$_3$ filtered	Temp. of reactor °C	Number recycles	Reaction time per recycle min	Mole ratio water to TNT	Red water from run no.	Vol. red water mL	Temp. MgSO$_3$ dissolver °C	PRODUCT ANALYSIS						
														DNT 2,6 and	DNT 2,4	DNT TOTAL	TNT 2,4,6	META ISOMERS 2,4,5 and	META ISOMERS 2,3,4	META ISOMERS TOTAL
G-8	12.24:1	80.26	8.6	0	100	No	82	N/A	15	12.4:1	N/A	0	N/A			0.10	99.62			0.28
G-9	14.02:1	79.62	8.7	"	"	"	82	"	"	"	"	"	"			0.11	98.65			1.24
G10	16.02:1	79.98	8.6	"	"	"	82	"	"	"	"	"	"			0.11	99.31			0.58
G11	12.36:1	79.76	7.5	"	"	"	80	"	"	"	"	"	"			0.11	98.89			1.00
G12	14:1	79.30	7.5	"	"	"	81	"	"	"	"	"	"			0.10	98.44			1.46
G13	16:1	79.67	7.5	"	"	"	80	"	"	"	"	"	"			0.12	98.80			1.09
G14	12.06:1	80.07	9.6	"	"	"	"	"	"	"	"	"	"			0.11	99.40			0.49
G15	14:1	80.00	9.0	"	"	"	"	"	"	"	"	"	"			0.11	99.41			0.48
G16	16:1	79.51	8.9	"	"	"	"	"	"	"	"	"	"			0.10	98.54			1.35
G17	18:1	79.74	8.8	"	"	"	"	"	"	"	"	"	"			0.10	98.83			1.05
G18	20:1	79.80	8.8	"	"	"	"	"	"	"	"	"	"			0.10	98.94			0.97
G19	12.18:1	80.21	8.8	"	"	"	"	"	"	"	"	"	"			0.10	99.61			0.29
G20	11:1	80.37	8.9	"	"	"	"	"	"	"	"	"	"			0.11	99.63			0.26
G21	10:1	80.05	8.6	"	"	"	"	"	"	"	"	"	"			0.10	99.14			0.76
G22	9:1	80.42	8.6	"	"	"	"	"	"	"	"	"	"			0.10	99.90			--
G23	8:1	80.42	8.8	"	"	"	"	"	"	"	"	"	"			0.10	99.70			0.20
G24	7:1	80.52	8.75	"	"	"	"	"	"	"	"	"	"			0.10	99.90			--
G25	6:1	80.42	8.75	"	"	"	"	"	"	"	"	"	"			0.10	99.57			0.33
G26	7.5:1	80.48	8.9	"	"	"	"	"	"	"	"	"	"			0.10	99.77			0.12
G40	6:1	80.26	7.5-8.2	"	"	"	"	"	"	"	"	"	"			0.09	99.75			0.16
G41	5:1	80.24	7.5-8.5	"	"	"	"	"	"	"	"	"	"			0.09	99.66			0.24
G42	4:1	80.38	7.5-8.7	"	"	"	"	"	"	"	"	"	"			0.10	99.84			0.05
G43	7:1	80.06	7.5-8.2	"	"	"	"	"	"	"	"	"	"			0.10	99.34			0.57
R-1	10.2:1	80.10	5.0-8.5	"	500	Yes	85	5	5	"	"	"	85	0.01	0.06		99.66	0.02	0.25	
R-2	17.6:1	79.11	7.2-8.3	"	"	"	85	"	"	"	"	"	"	0.01	0.06		97.88	1.55	1.00	
R-3	10.1	79.76	7.3-8.4	"	"	"	—	"	"	"	"	"	--	0.01	0.05		99.79	0.00	0.11	
R-4	10:1	<79	--	"	"	-	--	"	"	70:1	"	"	--	0.02	0.05		97.98	1.08	0.87	
R-5	10:1	80.07	6.5-8.3	"	"	"	83	"	"	"	"	"	90	0.02	0.05		99.36	0.25	0.32	
R-6	10:1	80.46	7.9-8.3	"	"	"	"	"	"	"	"	"	84	0.02	0.07		99.91	0.00	0.00	
R-7	10:1	80.46	7.1-8.3	"	"	"	"	"	"	"	"	"	86	0.03	0.06		99.90	0.00	0.01	
R-8	15:1	80.13	7.2-8.0	"	"	"	92	"	"	"	"	"	"	0.03	0.07		99.48	0.08	0.35	
R-9	12:1	80.44	7.5-8.4	"	"	"	83	"	"	"	"	"	81	0.02	0.06		99.91	0.00	0.01	
R10	14:1	80.24	6.1-8.5	"	"	"	84	"	"	"	"	"	82	0.02	0.07		99.64	0.04	0.23	
R11	14:1	80.42	8.2	"	"	No	86	0	30	"	"	"	"	0.03	0.05		99.91	0.00	0.01	
R12	17:1	80.39	7.9	"	"	"	"	"	23	"	"	"	"	0.02	0.05		99.86	0.00	0.06	
R13	25:1	79.09	6.5-5.1	"	"	"	87	"	25	"	"	"	"	0.02	0.06		97.90	1.05	0.97	
R14	20:1	79.89	7.4-6.6	"	"	"	85	"	"	"	"	"	"	0.02	0.06		99.20	0.25	0.47	
R15	20:1	79.77	7.4-6.8	"	"	"	83	"	"	"	"	"	"	0.02	0.05		98.94	0.40	0.58	
R16	14:1	80.27	6.8-8.0	4	"	Yes	"	5	5	"	"	"	79	0.02	0.06		99.69	0.03	0.20	
R17	14:1	80.26	6.5-8.1	6	"	"	82	"	"	"	"	"	82	0.02	0.06		99.60	0.10	0.21	
R18	14:1	79.99	6.3-7.7	15	"	"	83	"	"	"	"	"	78	0.02	0.05		99.30	0.29	0.34	
R19	10:1	79.85	6.2-7.8	"	"	"	82	"	"	"	"	"	72	0.02	0.05		99.03	0.50	0.39	
R20	10:1	79.98	6.3-7.8	10	"	"	"	"	"	"	"	"	84	0.02	0.06		99.14	0.40	0.37	

Table 2. (cont)

Run no.	Mole ratio TNT to $MgSO_3$	Set point °C	pH reactor	%$MgSO_4$ added	Total vol. of water mL	$MgSO_3$ filtered	Temp. of reactor °C	Number recycles	Reaction time per recycle in	Mole ratio water to TNT	Red water from run no.	Vol. red water mL	Temp. $MgSO_3$ dissolver °C	DNT 2,6	and 2,4	TNT 2,4,6	META ISOMERS 2,4,5	and 2,3,4
R21	10:1	80.03	6.3-7.9	10	500	Yes	81	5	5	70:1	N/A	0	88	0.02	0.05	99.28	0.33	0.32
R22	10:1	80.42	6.8-8.1	5	"	"	82	"	"	"	"	"	75	0.02	0.05	99.82	0.03	0.07
R23	10:1	80.18	6.6-8.0	10	"	"	"	"	"	"	"	"	84	--	--	--	--	--
R24	10:1	80.39	6.8-8.0	7.5	"	"	"	"	"	"	"	"	82	0.02	0.06	99.76	0.05	0.09
R25	10:1	80.23	6.6-7.9	9.8	"	"	83	"	"	"	"	"	83	0.02	0.06	99.54	0.16	0.21
R26	10:1	80.24	7.0-7.8	8	250	"	"	"	"	35:1	"	"	83	0.02	0.05	99.82	0.00	0.12
R27	10:1	80.24	6.9-8.0	8	"	"	"	"	"	"	"	"	76	0.02	0.05	99.67	0.10	0.16
R28	10:1	80.18	7.0-7.8	10	500	"	82	"	"	70:1	"	"	81	0.03	0.08	99.74	0.04	0.11
R29	14:1	80.33	6.8-8.0	10	"	"	"	"	"	"	"	"	74	0.02	0.04	99.74	0.07	0.13
R30	14:1	80.10	6.8-7.9	10	"	"	84	"	"	"	"	"	68	0.03	0.05	99.50	0.16	0.26
R31	14:1	80.08	7.1-7.9	10	"	"	83	"	"	"	"	"	68	0.03	0.07	99.48	0.14	0.26
R32	14:1	79.68	7.1-7.6	14	"	"	81	"	"	"	"	"	68	0.02	0.06	98.75	0.64	0.53
R33	14:1	79.99	7.3-7.8	13	"	"	82	"	"	"	"	"	70	0.02	0.05	99.30	0.32	0.30
R34	14:1	79.95	7.0-7.8	13	"	"	83	"	"	"	"	"	71	0.03	0.06	99.27	0.34	0.31
R35	10:1	80.26	7.0-7.9	10	"	"	81.2	"	"	"	"	"	66	0.02	0.06	99.66	0.05	0.21
R36	14:1	79.85	6.8-7.8	10	"	"	82.2	"	"	"	"	"	71	0.02	0.08	99.53	0.16	0.22
R37	10:1	80.27	7.1-7.9	10	"	"	81.7	"	"	"	"	"	70	0.02	0.06	99.76	0.05	0.10
R38	14:1	80.09	7.1-7.8	10	"	"	82.8	"	"	"	"	"	63	0.02	0.08	99.58	0.13	0.19
R39	14:1	80.06	6.5-7.7	10	"	"	94.2	"	"	"	"	"	83	0.02	0.07	99.55	0.15	0.20
R40	14:1	79.84	6.5-8.0	10	"	"	77.2	"	"	"	"	"	45	0.02	0.08	99.21	0.33	0.35
R41	14:1	80.16	6.7-7.6	10	"	"	91.2	"	"	"	"	"	83	0.01	0.14	99.65	0.07	0.12
R42	14:1	79.86	6.6-7.4	15	"	"	91.0	"	"	"	"	"	76	0.01	0.17	99.15	0.37	0.30
R43	10:1	80.28	7.0-7.7	10	"	"	91.4	"	"	"	"	"	70	0.01	0.17	99.72	0.03	0.06
R44	10:1	80.08	6.9-7.6	15	"	"	91.4	"	"	"	"	"	75	0.01	0.16	99.50	0.15	0.17
R45	10:1	80.05	6.8-7.5	15	"	"	91.1	"	"	"	"	"	72	0.03	0.15	99.32	0.22	0.27
R46	14:1	80.24	6.8-7.7	6	"	"	92.3	"	"	"	"	"	72	0.04	0.14	99.72	0.02	0.08
R47	14:1	80.30	7.2-7.8	6	"	"	92.5	"	"	"	"	"	73	0.01	0.15	99.83	0.00	0.01
R48	8:1	80.21	7.1-7.8	12	"	"	83.8	"	"	"	"	"	63/86	0.01	0.15	99.78	0.03	0.03
R49	8:1	80.21	7.1-7.6	12	"	"	92.2	"	"	"	"	"	70/85	0.01	0.15	99.74	0.05	0.05
R50	14:1	80.16	7.8-7.6	8	"	No	92.3	0	25	"	"	"	89	0.01	0.16	99.65	0.06	0.11
R51	14:1	79.69	6.8-8.0	6	"	Yes	81.9	5	0	"	"	"	81/85	0.01	0.16	98.90	0.51	0.42
R52	14:1	80.04	6.9-7.9	6	"	"	82.9	3	5	"	"	"	60/80	0.01	0.17	99.43	0.17	0.22
R53	14:1	80.25	6.9-7.9	6	"	"	82.3	"	10	"	"	"	77	0.01	0.15	99.74	0.02	0.08
R54	14:1	79.76	7.3-7.9	6	"	"	82.4	3	3	"	"	"	63/77	0.01	0.15	99.13	0.38	0.33
R55	14:1	80.19	6.8-8.1	6	"	"	82.9	3	7	"	"	"	63/88	0.01	0.15	99.62	0.08	0.14
R56	8:1	80.39	6.9-8.2	8	400	"	82.7	5	5	56.1	"	"	60/80	0.01	0.15	99.80	0.00	0.03
R57	8:1	80.41	7.9-8.1	8	200	"	86.9	5	5	28:1	"	"	63/67	0.01	0.17	99.83	0.00	0.00
R58	8:1	80.40	7.8-8.1	8	200	"	89.7	5	5	28:1	"	"	63	0.01	0.16	99.83	0.00	0.00
R59	8:1	80.44	7.8-7.9	8	300	"	87.6	5	5	42:1	"	"	70	0.01	0.16	99.83	0.00	0.00
R60	8:1	80.41	7.8-8.1	8	250	"	87.9	5	5	35:1	"	"	70/77	0.01	0.16	99.81	0.00	0.01
R61	14:1	80.25	7.0-8.0	8	500	"	87.7	5	5	70:1	"	"	75/78	0.01	0.16	99.73	0.02	0.08
R62	14:1	80.34	7.9-8.3	8	500	"	87.7	5	5	70:1	"	"	79/84	0.01	0.16	99.79	0.00	0.03
R63	14:1	80.31	7.4-7.8	8	250	"	87.3	5	5	35:1	"	"	68/74	0.01	0.17	99.77	0.00	0.06
R64	14:1	80.24	7.5-7.6	0	200	"	90.0	3	5-5-15	28:1	50	170	76/80	0.01	0.16	99.70	0.01	0.11
R65	14:1	80.13	7.8-8.1	0	200	"	89.8	3	5-5-15	28:1	64	152	87	0.01	0.16	99.63	0.03	0.16

Table 2. (cont)

Run no.	Mole ratio TNT to MgSO$_3$	Set point °C	pH reactor	%MgSO$_4$ added	Total vol. of water mL	MgSO$_3$ filtered	Temp. of reactor °C	Number recycles	Reaction time per recycle in	Mole ratio water to TNT	Red water from run no.	Vol red water mL	Temp. MgSO$_3$ dissolver °C	PRODUCT ANALYSIS DNT 2,6	and 2,4	TNT 2,4,6	META ISOMERS 2,4,5,	and 2,3,4,
R66	14:1	80.25	7.5-7.7	0	200	Yes	91.3	3	5-5-15	28:1	65	140	73	0.01	0.16	99.78	0.00	0.04
R67	14:1	80.27	7.7-8.0	0	200	"	90.0	5	5	28:1	66	142	61/75	0.01	0.16	99.77	0.00	0.05
R68	14:1	80.24	7.6-7.9	0	200	"	90	5	5	28:1	67	144	64/75	0.01	0.16	99.77	0.00	0.05
R69	8:1	80.45	7.5-8.4	6	500	"	92	3	5	70:1	-	0	63/72	0.01	0.16	99.81	0.00	0.01
R70	8:1	80.43	7.5-8.0	6	500	"	92	3	5	70:1	-	0	55/64	0.01	0.16	99.79	0.01	0.03
R71	8:1	79.90	7.2-7.9	6	500	"	88	3	3	70:1	-	0	69/74	0.01	0.16	99.14	0.36	0.33
R72	8:1	80.13	7.5-8.0	6	500	"	87	3	3	70:1	-	0	50/73	0.01	0.15	99.39	9.22	0.24
R73	10:1	79.93	7.1-8.1	6	500	"	88	2	3	70:1	-	0	55/67	0.01	0.15	99.53	0.13	0.18
R74	10:1	80.09	7.2-7.9	6	500	"	87	3	3	70:1	-	0	67/76	0.01	0.16	99.37	0.22	0.23
R75	14:1	80.23	7.4-7.7	0	200	"	89	3-1	5-10	28:1	68	146	60/64	0.01	0.13	99.81	0.00	0.04
R76	14:1	80.27	6.8-7.8	6	500	"	92	5	5	70:1	-	-	54/71	-	-	-	-	-
R77	8:1	80.47	7.1-7.9	6	500	"	91	5	5	70:1	-	-	58/76	-	-	-	-	-
R78	14:1	80.26	6.7-7.7	6	500	"	87	5	5	70:1	-	-	54/78	-	-	-	-	-
R93	10:1	80.40	7.4-8.3	6	500	"	85	5	5	70:1	-	-	56/80	0.01	0.11	99.87	0.00	0.01
R94	10:1	80.28	6.7-8.2	6	500	"	84	5	5	70:1	-	-	64/75	0.01	0.08	99.78	0.03	0.10
R95	14:1	80.28	7.5-8.4	0	500	"	87	5	5	70:1	-	-	58/87	0.01	0.13	99.76	0.01	0.09

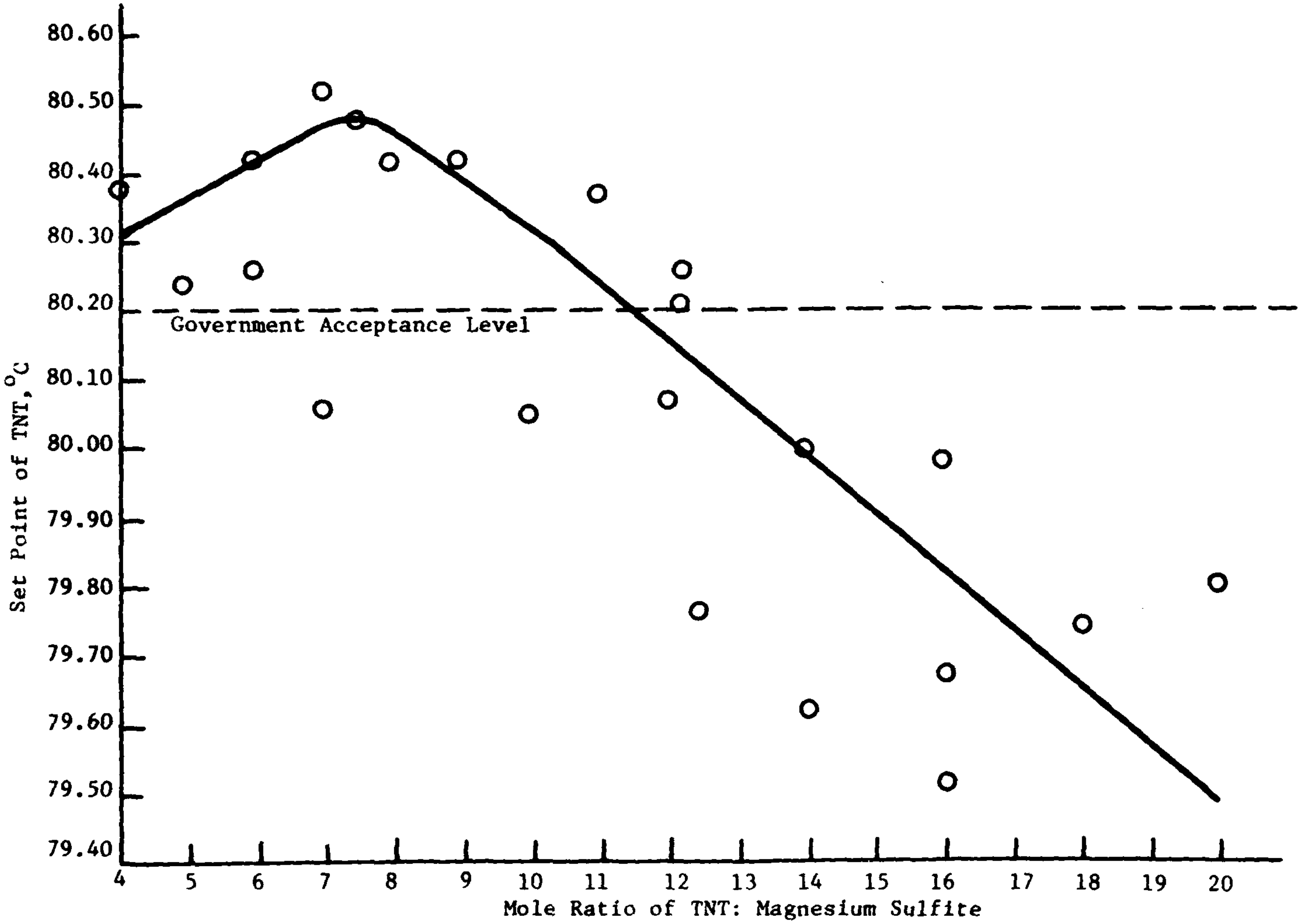


Figure 1. Effect of mole ratio of TNT to magnesium sulfite hexahydrate on set point of treated crude TNT

The recycle investigation employed the same laboratory reaction vessel and auxiliary equipment as in the previous runs. To prevent the solid $MgSO_3$ from contaminating the TNT, the $MgSO_3$ was added to hot water in a separate vessel mounted on a magnetic stirrer hot plate (see figure 2). The water layer, saturated with $MgSO_3$, was pumped through a filter into the reaction vessel. After rapid stirring at various reaction times, the phases were allowed to settle. The red water layer was pumped back to the dissolver to dissolve additional $MgSO_3$ and the cycle repeated several times. The temperature of the dissolver was maintained at 70-80°C to prevent the $MgSO_3$ from changing from the hexahydrate to the less reactive trihydrate form.

After the final recycle of the $MgSO_3$, the red water was decanted from the molten TNT in the reaction vessel. Three hundred mL of boiling distilled water was added to the reaction vessel followed by stirring. After stirring for 5 minutes, the two phases were allowed to separate and the water decanted. Washing was repeated two additional times.

The first five runs, R-1 through R-5, (see table 2) were washed in this manner but reproducible set points could not be obtained from TNT purified using the same conditions. Starting with R-6 the pH of the wash water was adjusted from pH 8 to 7 using a weak H_2SO_4 solution. The second and third washes were also adjusted to pH 7 but very little H_2SO_4 was required. The reduction in pH not only resulted in reproducible set points but also increased the rate of phase separation.

After the last wash water had been decanted the molten TNT was poured into two test tubes which were then placed in a glycerin bath held at 100°C. When the TNT had remelted the separated water was removed with a medicine dropper and an air sparge inserted to dry the molten TNT. A set point was run on each tube and a sample was prepared for gas chromatographic analysis.

Effect of Magnesium Sulfate Build Up

During the purification reaction, magnesium sulfate ($MgSO_4$) is formed due to air oxidation. To determine the effect of $MgSO_4$ on the purification process various runs were made with $MgSO_4$ added to the water in the reactor at the start of the purification. Figure 3 shows the effect of the added $MgSO_4$ on the set point of TNT purified at two mole ratios of TNT to $MgSO_3$.

The maximum permissible level of $MgSO_4$ at a 10:1 mole ratio is approximately 11 percent and 6 percent at a 14:1 mole ratio. The percentage of $MgSO_4$ is based on the amount in the volume of water used for purification in the reaction vessel and the $MgSO_3$ dissolver.

Effect of Reaction Time

The next parameter investigated was purification reaction time. A mole ratio of 14:1 TNT to $MgSO_3$ with 6 percent added $MgSO_4$ was chosen

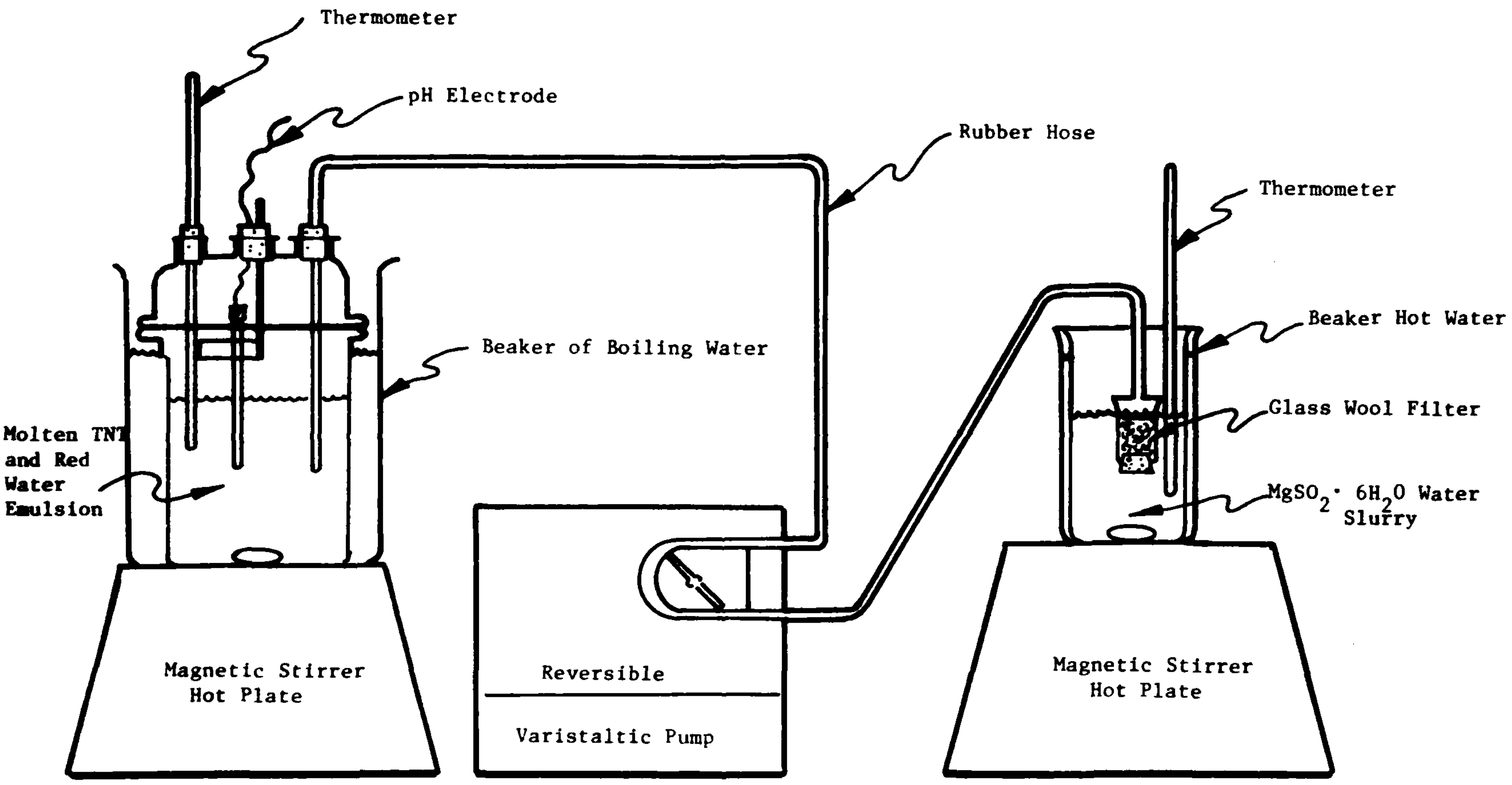


Figure 2. Laboratory TNT purification apparatus

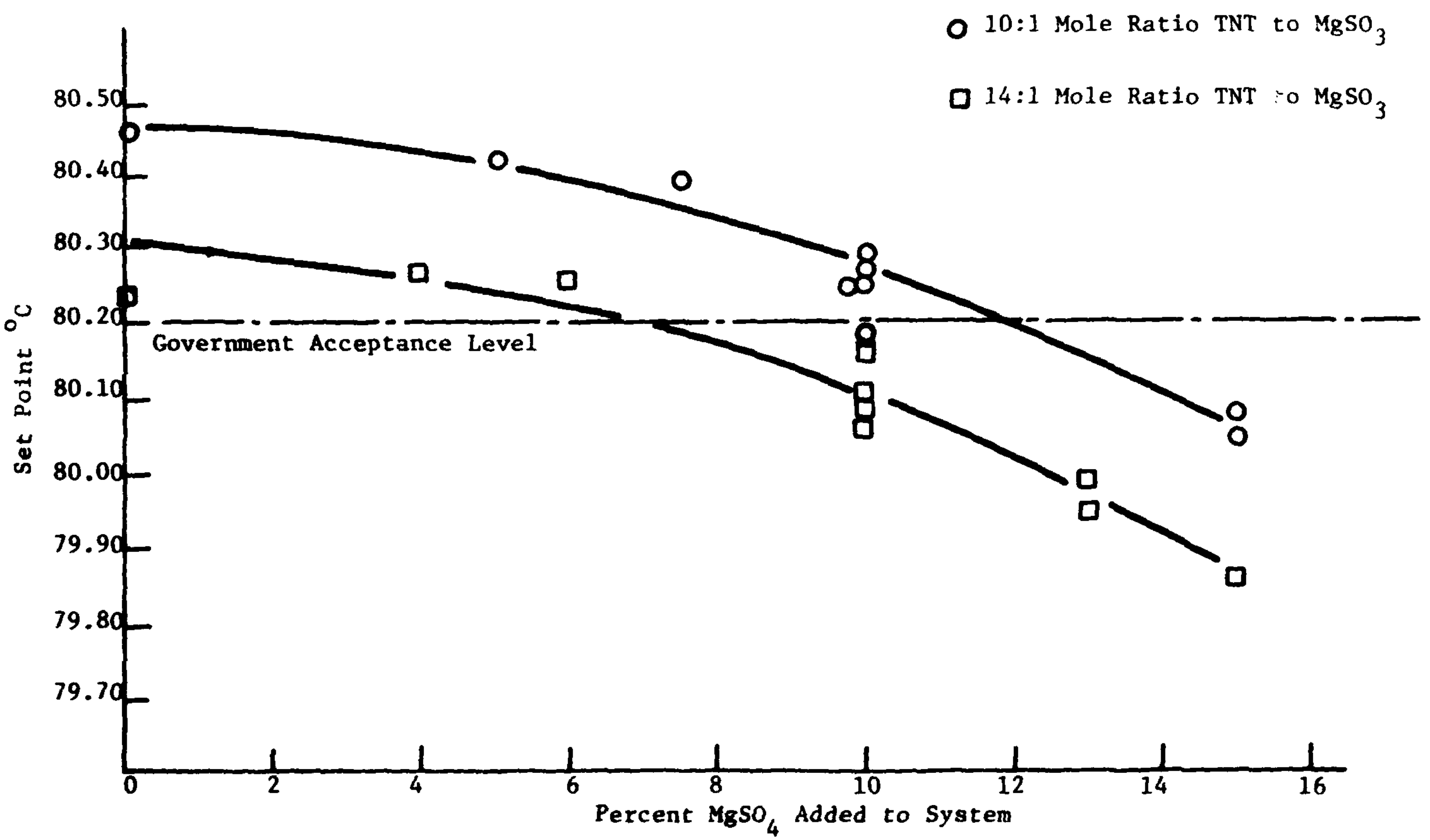


Figure 3. TNT set point versus percent $MgSO_4$

for this series because the values are the most marginal in producing TNT with a set point above 80.20. During the majority of the runs, the red water was recycled five times from the purification vessel to the dissolver with a five minute reaction time in between each recycle. During the transfer of 200 mL of red water from the purification vessel to the $MgSO_3$ dissolver, the TNT and red-water mixture was not stirred. Consequently, the two phases were not in contact, except at the interface of the two immiscible liquids in the reactor. After the red water was refortified with $MgSO_3$, it was transferred through the filter back to the purification vessel and the red water TNT mixture was stirred with maximum agitation. The reaction times are the period of stirring between the completion of the transfer of the $MgSO_3$ solution to the purification vessel and the start of the red water to the $MgSO_3$ slurry vessel. A graph of the data is shown in figure 4. The number of recycles can be variable as long as the total reaction time remains greater than 22 minutes.

Previously, reaction times had been based only on the stirring time of the TNT and $MgSO_3$. The times represented in figure 5 are the total contact time between the TNT and $MgSO_3$ which includes the time for recirculation of the red water as well as mixing time. All other conditions were constant. The reaction time at the 14:1 ratio for a set point of 80.20°C is 25 minutes compared to 13 minutes for the 8:1 ratio.

Effect of Mole Ratio of Water to TNT

A limited study was conducted to determine the effect of reducing the mole ratio of water to TNT in the purification reaction. The majority of runs were made at a phase mole ratio of 70:1 but the ratio can be reduced to 28:1 and still produce TNT with acceptable set points and reduce the amount of in-process water. See table 2 for test results.

Effect of Red Water Reuse

The next phase of investigation was the effect of reusing red water as the aqueous phase in subsequent reactions to simulate production conditions where red water solids would build up. The 170 mL of red water remaining from Run R-50 was diluted to 200 mL with distilled water for use as the aqueous phase in Run R-64. The 200 mL of diluted red water was added to the molten TNT in the purification vessel for a phase mole ratio of 28:1. After a brief period of agitation, the aqueous phase was pumped to the dissolver where the $MgSO_3$ was added. The solution was then filtered and pumped to the purification vessel. The refortification was repeated three times. The reaction time was five minutes for the first two transfers and 15 minutes during the third transfer for a total reaction time of 25 minutes. The same approach was used for Runs R-65 through R-68 and R-75. The red water from R-64 was used for R-65 and the red water from R-65 for R-66, etc. The set points were above 80.20°C in all runs except R-65 and this may have been due to an excessively high temperature in the dissolver.

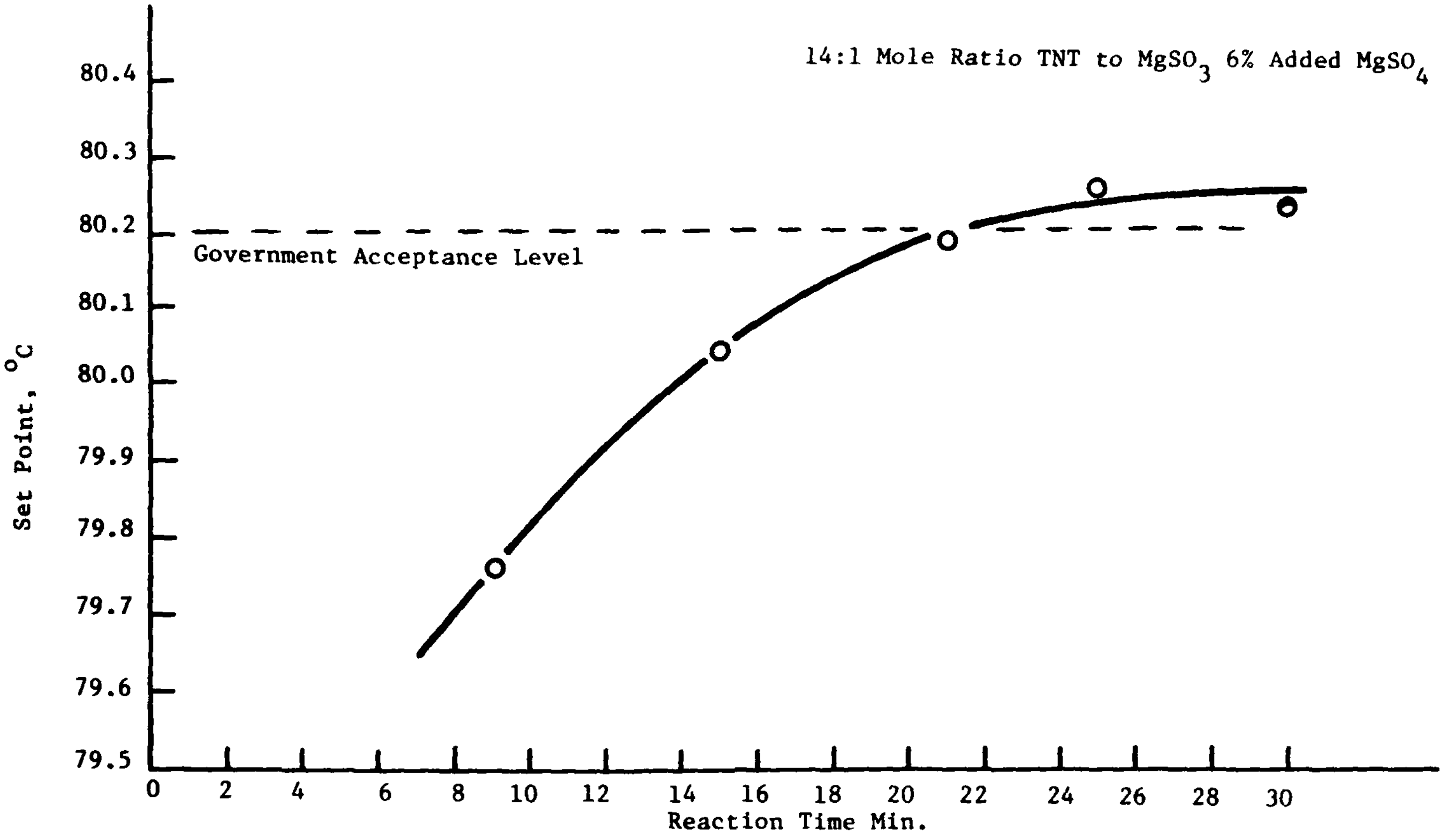


Figure 4. *TNT set point versus stirring time*

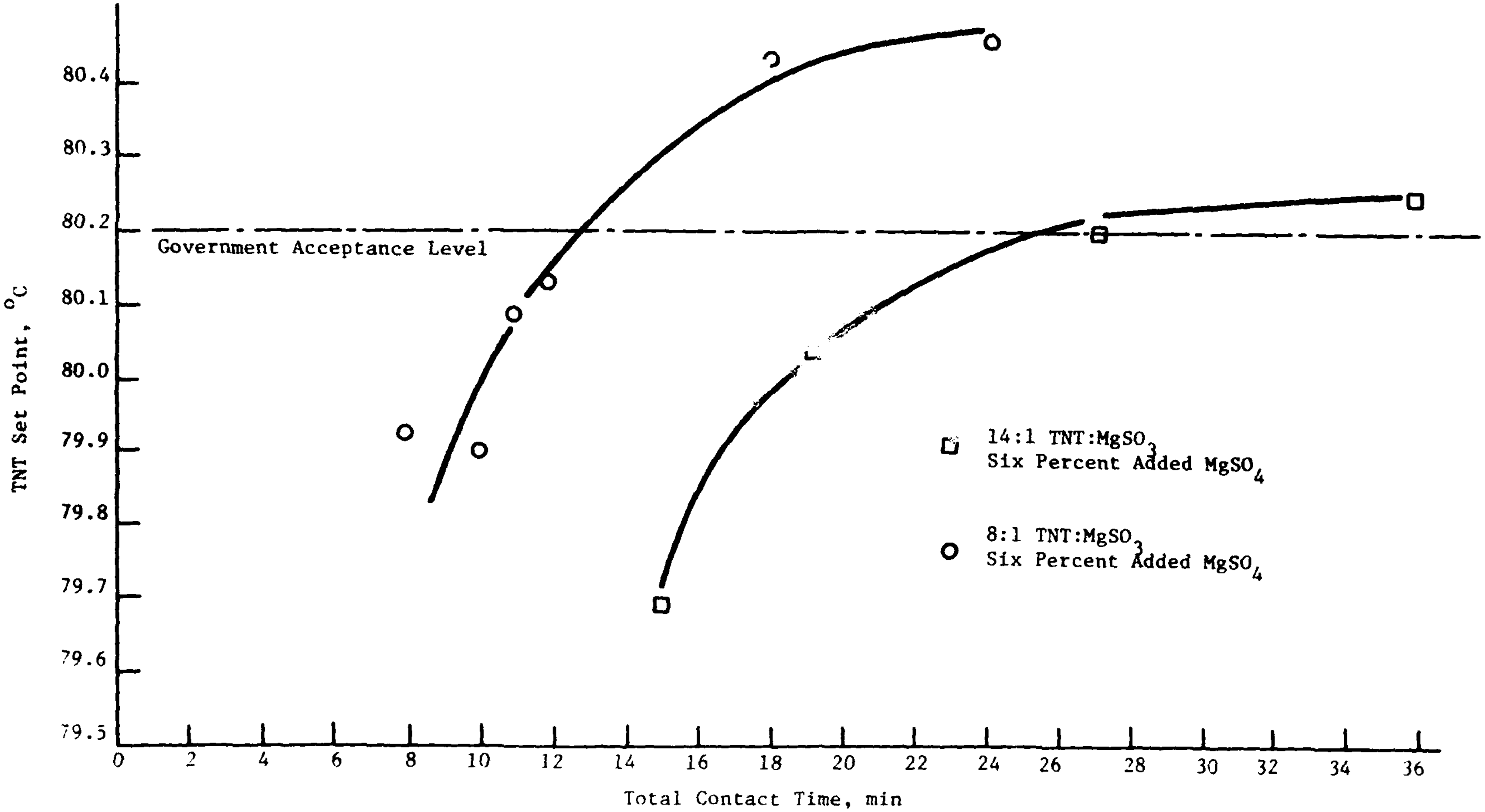


Figure 5. TNT set point versus reaction time

From the above data, it appears that red water can be used repeatedly when refortified with $MgSO_3$ and diluted with additional water. Gas chromatography (GC) analysis showed that the purified TNT from these six runs had the same composition. Thin layer chromatograpy showed a slight increase in the 3-methyl-2',4,4',6,6' pentanitrodiphenylmethane (MPDM) addition compound compared to TNT purified with the fresh $MgSO_3$. The purified TNT from Run 67 was analyzed for magnesium (Mg) and only 0.001 percent was found.

Effect of Magnesium Sulfite Solubility

The solubility of $MgSO_3$ as a function of temperature in a red water composite from three runs was determined. This was an important consideration due to the low solubility of $MgSO_3$ in distilled water, 1.65 g/100 mL at 70°C. The red water from Runs R-64, 70, and 74 was used for testing and a temperature range of 20 to 75°C was covered. The data is shown in Figure No.6 and table 3. From the data it is obvious that $MgSO_4$ and the soluble salts in red water considerably increase the solubility of $MgSO_3$ in aqueous solutions.

Investigation of Solid Separators in the Recycle Process

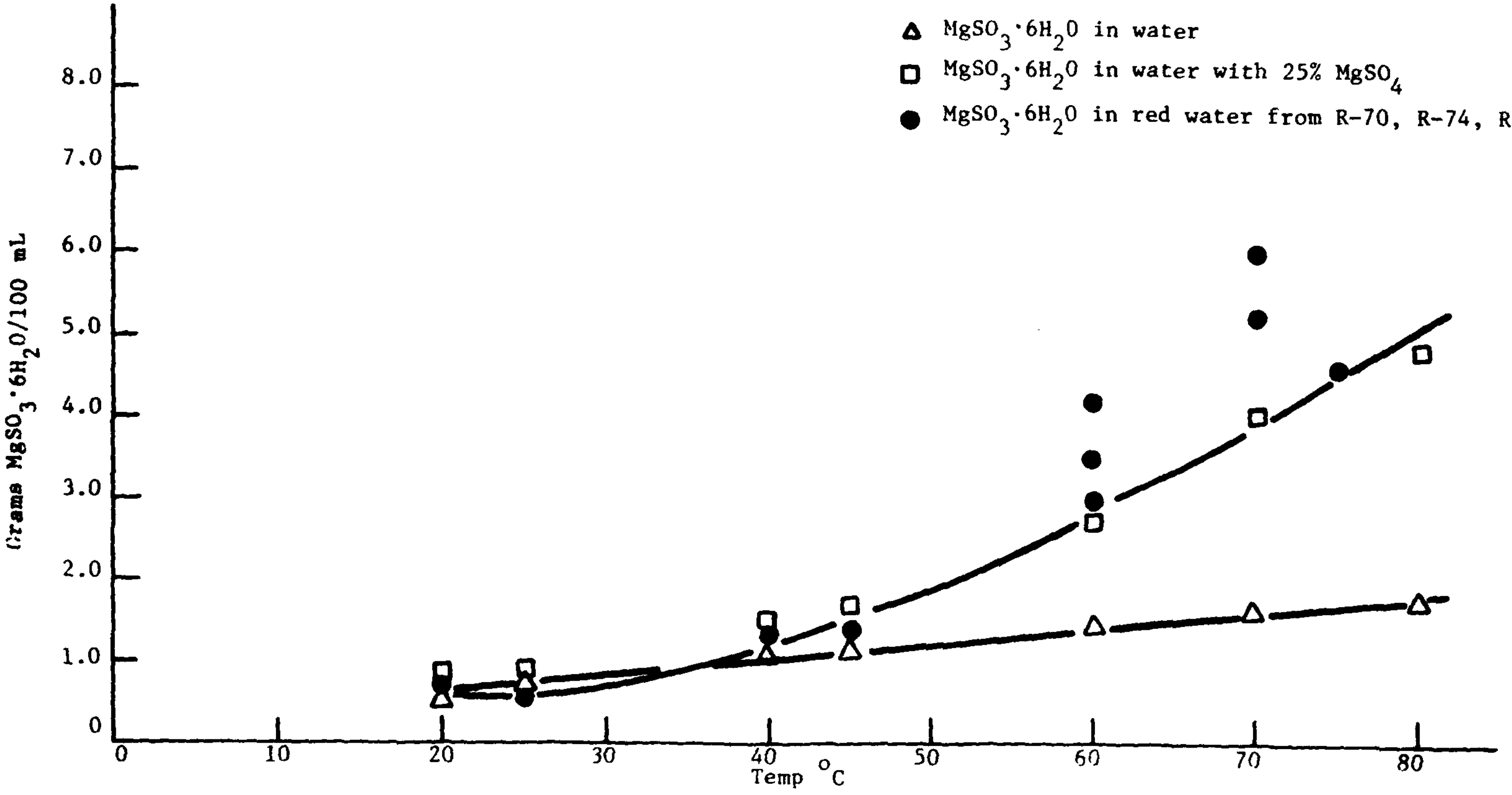
In the recycle process, particulate $MgSO_3$ must be removed from the recirculated red water prior to its being fed back into the purification vessels. A number of filteration approaches could be utilized in this system, however, the spent red water may also contain some TNT. In order to prevent filter pluggage with TNT and provide a simple and reliable system, two methods of separation were investigated. An additional advantage is that these systems could perhaps be mounted in the TNT Nitration and Purification (N&P) building thus precluding pumping of red water through the barricade to one of the support buildings.

The first approach used a small scale plastic compartmentalized clarifier vessel as shown in figure 7. Solid $MgSO_3$ was added to water in the first stirring compartment, which was heated to 55°C. Additions of a recycled feed solution to the first compartment permitted flow within the system.

The $MgSO_3$ settling rate was measured by determining the turbidity of the final solution with a Hach Turbidimeter. The compartmentalized clarifier did not efficiently remove $MgSO_3$ particles and was abandoned.

The second approach for the removal of $MgSO_3$ particles incorporated hydrocyclones. A laboratory evaluation of several glass hydrocyclones showed them to be the most effective separation approach.

The equipment arrangement for the use of hydrocyclones in the TNT process are presented in figures 8 and 9 for one and two mix tanks respectively. The data represents flows for a 70-ton per day rate using dynamic separator equipped purification vessels. The assumptions and calculated flows of both methods are presented with the following assumptions:



▲ $MgSO_3 \cdot 6H_2O$ in water

□ $MgSO_3 \cdot 6H_2O$ in water with 25% $MgSO_4$

● $MgSO_3 \cdot 6H_2O$ in red water from R-70, R-74, R-49

Figure 6. Solubility of magnesium sulfite hexahydrate in water and red water

Table 3. Solubility of $MgSO_3 \cdot 6H_2O$ in red water

Red water run no.	Mole ratio TNT: $MgSO_3$	Added $MgSO_4$ %	TNT set point °C	$MgSO_3 \cdot 6H_2O$ g/100 m							
				RW (1)	20°C	25°C	40°C	45°C	60°C	70°C	75°C
(2)					0.65	0.75	1.05	1.15	1.45	1.65	1.74
(3)					0.82	0.96	1.46	1.68	2.77	4.05	4.85
R-70	10:1	6	80.43	0.20	-	0.62	1.32	-	3.43	-	-
R-70	10:1	6	80.43	0.20	-	-	-	1.36	3.45	5.24	-
R-74	10:1	6	80.09	0.37	-	0.51	1.41	-	2.95	-	4.57
R-49	8:1	12	80.21	0.12	0.66	-	1.48	-	4.18	6.00	-

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(1) Red water analysis at room temperature without added $MgSO_3 \cdot 6H_2O$.

(2) Solubility $MgSO_3 \cdot 6H_2O$ in water.

(3) Solubility $MgSO_3 \cdot 6H_2O$ in water with 25% $MgSO_4$.

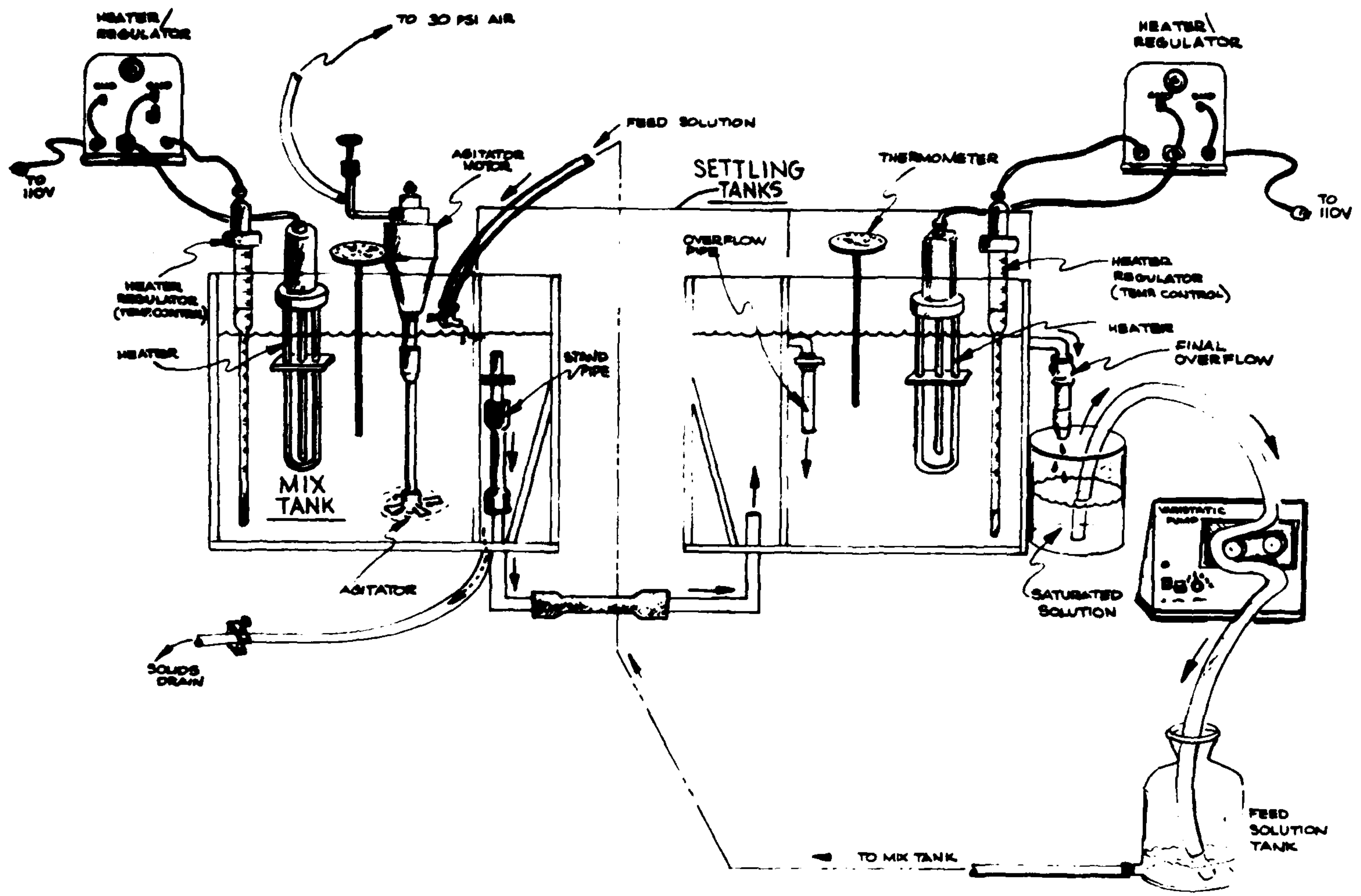

Figure 7. Clarification test apparatus

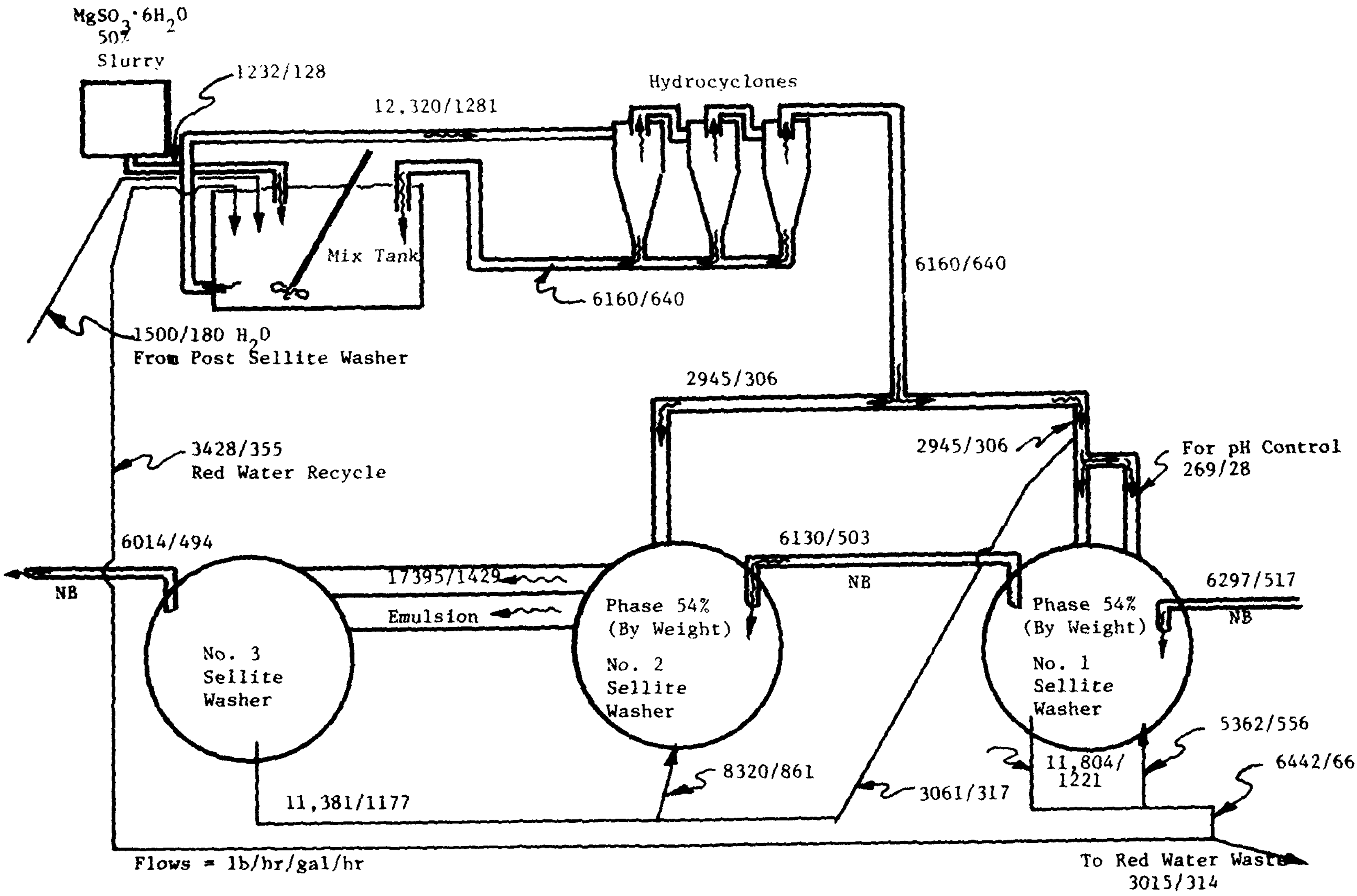

Figure 8. Simultaneous $MgSO_3$ addition configuration

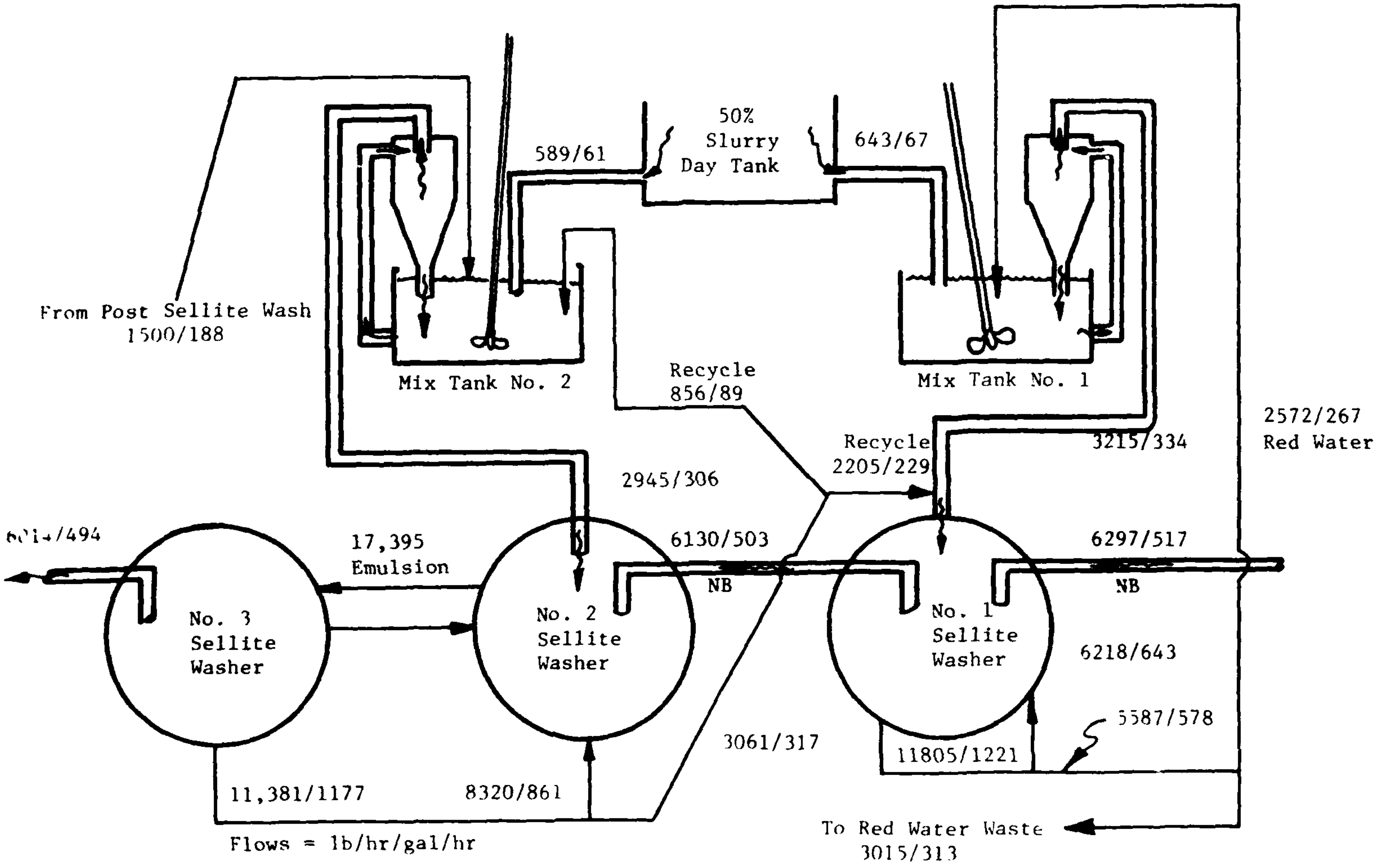

Figure 9. Countercurrent $MgSO_3 \cdot 6H_2$ addition configuratio

1. The washers will contain approximately 30 percent nitrobody by volume.

2. The nitrobody entering washer No. 1 will contain approximately 0.03 percent acidity.

3. Approximately 270 pounds per hour of a 10 percent solution of $MgSO_3$ are required for pH control of washer No. 1.

4. The nitrobody entering the No. 1 washer will contain approximately 3.8 percent meta-isomers and approximately 0.5 percent oxidation products. Approximately one-half of the meta-isomers will be removed in the No. 1 washer. The remaining meta-isomers will be reduced to a 0.25 percent concentration or lower in the No. 2 and No. 3 washers.

5. Also, approximately 0.5 percent of the TNT will be lost to the red water in the No. 1 washer. The aromatic content of the red water should be from 1.5 to 2 percent.

6. The $MgSO_3$ will be fed from a day tank to the dissolver as a 50 percent slurry.

In the first equipment arrangement as shown in figure No. 8, one $MgSO_3$ mix tank simultaneously feeds both washer No. 1 and 2. This approach will constrain the recirculated solution from the No. 2 and No. 3 washers to have the same salt concentration as the red water exiting the process.

The second method is to use two separate mix tanks in a countercurrent arrangement as shown in figure 9. The No. 2 and No. 3 washers are expected to be more efficient since the recirculated red water will be cleaner, i.e., contain less total salt in solution. A portion of this water can be fed to the No. 1 washer recirculation system when the red water increases substantially in total salt content before being discharged to waste. The countercurrent arrangement is significantly more efficient than the simultaneous feed arrangement, however, additional equipment cost would be realized.

Exudation and Linear Crystallization Studies

An exudation study was conducted on various TNT samples after drying via air sparging in a 100°C glycerin bath for four hours. The TNT was allowed to cool in the test tube and the cylinder of TNT removed and cut into 2-inch lengths. The cylinders of TNT were wrapped with filter paper and sealed in an aluminum tube. The sample was then placed in a 71°C oven for 68 hours. The filter paper was removed and the loss in weight of the TNT cylinder effectively permitted a calculation of the percent exudation.

The data obtained from the exudation study is shown in table 4 and figure 10. From the data it is obvious that there is no correlation between set point and percent exudation.

The linear crystallization velocity (LCV) was obtained on a dried sample as well. The molten TNT was drawn up into a 8 cm long section of thin wall capillary tubing and placed in a constant temperature bath. The LCV was measured over a 2 cm distance while immersed in a constant temperature bath. Figure 11 and table 5 illustrate the effect of bath temperature on the LCV and the relationship of TNT purified with $MgSO_3$, literature values for pure TNT and TNT manufacture at VAAP. All samples tested showed the same LCV relationship with bath temperature but the effect of set point was not significant. No significant difference in LCV was observed between TNT purified with $MgSO_3$ and Na_2SO_3.

Red Water Incineration Studv

In order to maintain a closed system in the purification of TNT with $MgSO_3$ the red water produced must be destroyed, and the $MgSO_3$ recovered. The first step in this process would be the incineration of red water to MgO. The sulfur dioxide (SO_2) released from incineration is absorbed in the recovered MgO slurry to form $MgSO_3 \cdot 6H_2O$.

The red water from several $MgSO_3$ purification runs were combined and evaporated to a total solids of 33.6% which is approximately the solids concentration expected before an incineration step can be performed. The analysis of the red water was as follows:

Analysis	Results, %
Solids (135°C)	34.62
Solids (939°C)	28.82
Sulfate as $SO_4^{=}$	20.58
Magnesium as Mg	5.53

Water is the volatile material when the sample is dried at 135°C. Nitrobodies and water of hydration are the main volatile components during burning at 939°C.

The samples for the incineration study were prepared by drying one mL of red water at 135°C for one hour in a porcelain crucible and grinding the solids with a glass rod. The appropriate weight of reducing agent (carbon) was then mixed with the solids and the mixture incinerated at the indicated temperature. The residue was dissolved in 1:1 hydrochloric acid and the residual sulfates determined using a barium sulfate precipitation method.

From the data shown in tables 6 and 7 the most suitable sources of reducing agents for $MgSO_4$ conversion are No. 6 fuel oil, sawdust and petroleum coke. The optimum weight ratio for all three sources is 0.187:1.

Table 4. Summary of exudation testing

Sample run no.	Set point °C	Exudation %	Purification type
50	80.22	1.72	Mg
59	80.35	0.83	Mg
52	79.78	1.44	Mg
65	80.01	1.02	Mg
55	80.19	2.62	Mg
75	80.21	1.89	Mg
62	80.32	1.84	Mg
69	80.45	1.12	Mg
74	80.06	3.88	Mg
76	80.20	2.13	Mg
47	80.35	0.77	Mg
58	80.45	2.17	Mg
70	80.44	0.50	Mg
53	80.26	1.23	Mg
103	80.48	1.00	Na
84	80.08	2.44	Na
95	80.37	2.80	Na
80	79.92	1.69	Na
60	80.50	2.18	Mg
63	80.41	1.04	Mg
49	80.31	2.94	Mg
72	80.11	3.03	Mg
73	80.02	3.52	Mg
97	80.44	0.35	Na
89	80.35	3.14	Na
85	80.21	3.92	Na
92	79.94	2.64	Na

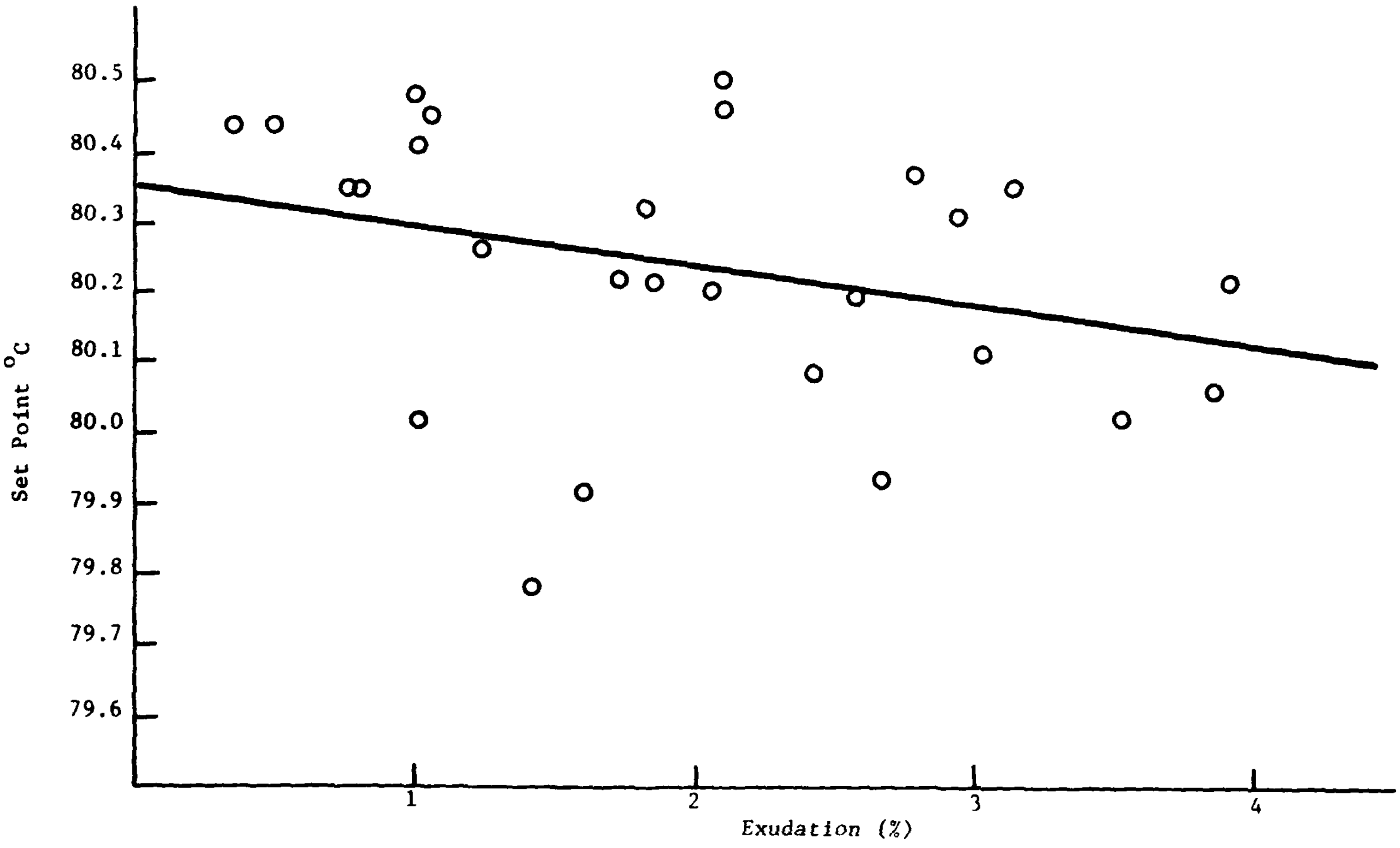

Figure 10. Relationship of exudation to set point

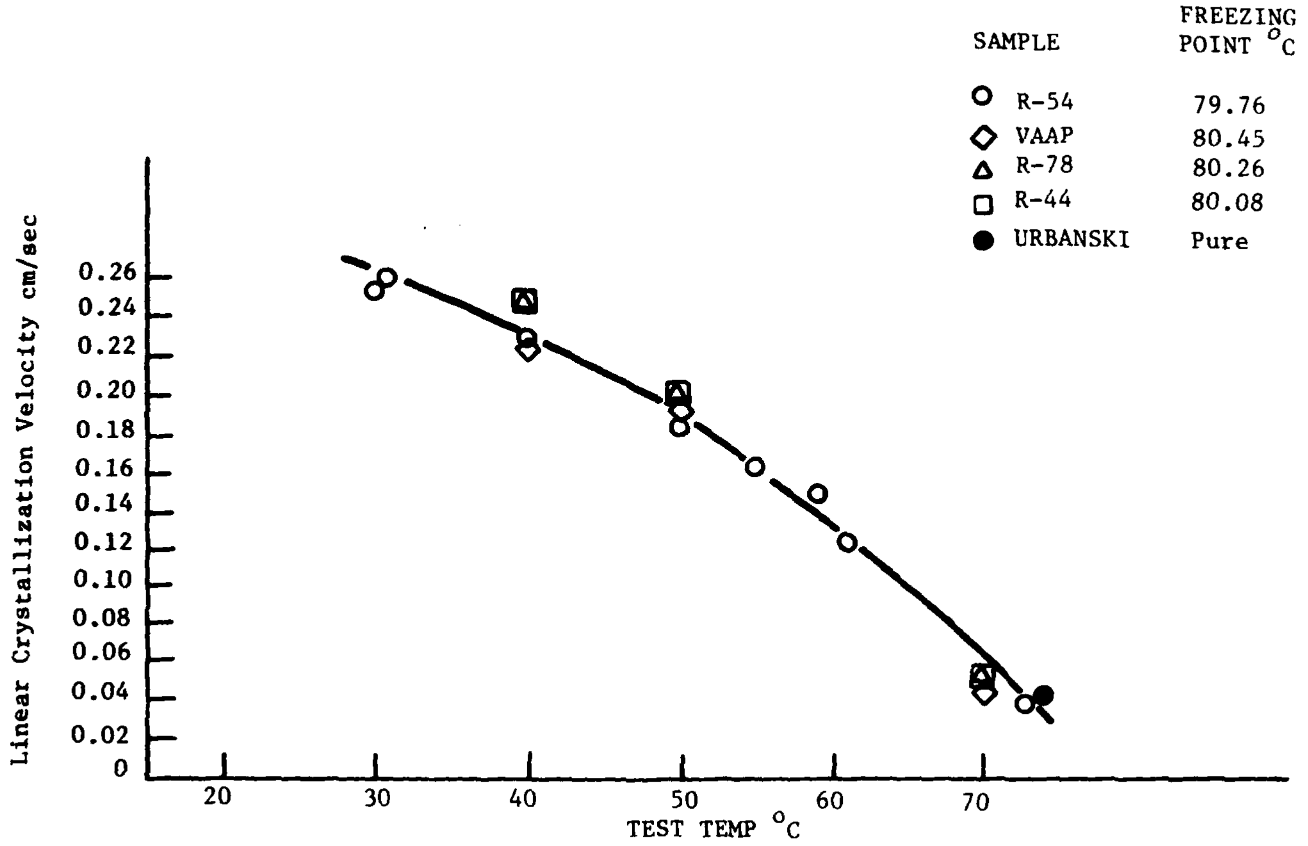

Figure 11. Relationship of linear crystallization velocity and testing temperature

Table 5. Summary of linear crystallization velocity at various temperatures

Sample	Set point °C	Bath temp °C	L.C.V. cm/min	L.C.V. cm/sec
Pure TNT [1]	-	74	2.5	0.042
VAAP [2]	80.45	40	13.6	0.227
		50	11.3	0.188
		70	2.5	0.042
R-44	80.08	40	14.9	0.248
		50	12.3	0.205
		70	3.0	0.050
R-54	79.76	30	15.2	0.253
		40	13.8	0.230
		50	11.2	0.187
		55	9.9	0.165
		59	8.9	0.148
		61	7.4	0.123
		70	2.7	0.045
R-64	80.24	50	12.0	0.200
R-66	80.25	50	9.5	0.158
R-71	79.90	50	10.7	0.178

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[1] Urbanski, The Chemistry and Technology of Explosives, Pergamon Press, 1965.

[2] Production samples

Table 6. Conversion of magnesium sulfate in red water(1)

Carbon Source	Weight ratio carbon: $MgSO_4$	Drying oven temp. °C	Furnace temp. °C	Remaining $MgSO_4$ %	Conversion %
#6 Fuel Oil	3:1	135	815	0.61	97.47
#6 Fuel Oil	1.5:1	135	815	0.31	98.79
#6 Fuel Oil	0.75:1	135	815	0.21	99.19
" "	3:1	135	927	0.00	100.00
" "	0.375:1	135	815	0.22	99.15
" "	0.375:1	135	704	3.19	87.63
" "	0.187:1	135	815	1.46	94.34
" "	0.094:1	135	815	8.43	67.31
Sawdust	0.75:1	135	815	0.38	98.53
"	0.094:1	135	815	6.50	74.80
"	0.187:1	135	815	0.47	98.18
Petroleum coke	0.187:1	135	815	9.35	63.75
" "	0.375:1	135	815	1.57	93.91
" "	0.375:1	135	927	0.10	99.61
" "	0.187:1	135	927	0.10	99.61
" "	0.094:1	135	927	2.24	91.31
" "	0.047:1	135	927	6.51	74.76
Carbon Black	0.187:1	135	815	3.38	96.62
Charcoal	0.187:1	135	815	1.14	95.58
Graphite	0.187:1	135	815	9.98	61.69
None (2)	0:1	135	815	18.23	29.33
None	0:1	135	815	15.21	41.02
None (2)	0:1	135	815	17.82	30.90
None	0:1	135	815	16.56	35.79

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(1) Red water contained 25.79% $MgSO_4$ based on SO_4 analysis.

(2) Crucibles purged with nitrogen before being burned in furnace.

Table 7. Comparison of carbon sources

Carbon source	Ash content percent	Conversion of $MgSO_4$ at 0.187:1 weight ratio percent	Cost per pound
No. 6 Fuel Oil	0.23	94.34	0.073
Sawdust	0.22	98.18	0.052
Petroleum Coke	0.30	63.75(1)	0.056
Petroleum Coke		99.61(2)	
Carbon Black	0.38	86.89	0.37
Charcoal	12.58	95.58	0.55
Graphite	1.78	61.69	0.86

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(1) Furnace temperature 815°C

(2) Furnace temperature 927°C

A furnace temperature of 815°C is required with the exception of petroleum coke which requires a temperature of 927°C. The other three carbon sources, carbon black, charcoal and graphite, are not suitable because of either cost, low efficiency or high ash content.

A sufficient amount of reclaimed $MgSO_3$ was needed to assure that it would produce purified TNT which would meet all requirements of specification MIL-T-248C. Several 25 mL portions of the red water were evaporated to dryness and the resulting solids ground into a fine powder. A 5g portion of the solids was mixed with 0.717g of petroleum coke to produce a coke to $MgSO_4$ weight ratio of 0.193 to 1. The mixture was incinerated in a muffle furnace at 927°C for three hours. Several incinerations yielded 28g of MgO with no $MgSO_4$ detected.

Twenty five grams of the MgO were slurried in 500 mL of distilled water. The slurry was stirred while adding SO_2 until the pH dropped from 9.25 to 4.40. After reacting for one hour, a temperature rise from 23°C to 48°C was observed. The precipitate was filtered, washed with distilled water and dried at 70°C for four hours. The reaction produced 49.81g of $MgSO_3 \cdot 6H_2O$ with a purity of 91.76 percent. Microscopic examination of the $MgSO_3$ found no traces of MgO but some dehydrated $MgSO_3$ was present.

The reclaimed $MgSO_3$ was used to purify three samples of crude TNT and the conditions for Runs R-93, 94 and 95 are shown in table 2. The chemical analysis of the TNT from the three runs are reported in table 8. All three samples met all the specification requirements indicating that reclaimed $MgSO_3$ will produce acceptable TNT.

Table 8. Analysis of TNT purified with reclaimed $MgSO_3$

	R-93	R-94	R-95	MIL-T-248C Limits
Set Point, °C	80.40	80.28	80.28	80.20 Min.
Magnesium, %	0.0004	0.0006	0.0004	No limit
Acidity as H_2SO_4, %	0.0006	0.0006	0.0006	0.02 Max.
Insolubles, %	0.006	0.005	0.005	0.05 Max.
Purity, %	99.87	99.78	99.76	-
2,6 DNT, %	0.01	0.01	0.01	-
2,4 DNT, %	0.11	0.08	0.13	-
2,4,5 TNT, %	0.00	0.03	0.01	-
2,3,4 TNT, %	0.01	0.10	0.09	-

CONCLUSIONS

The first phase of investigation was the purification of crude TNT using $(NH_4)_2SO_3$. Generally, set points of the purified TNT were low and appear to be related to amino-DNT content. Previous studies under PE-503 indicate that a high pH during purification with $(NH_4)_2SO_3$ is conducive to the formation of amino-DNT's. Therefore, a series of runs were conducted which lowered the pH in the reactor from a range of 9.6 - 8.4 to a range of 7.7 to 7.0. The decreased pH significantly lowered the amino-DNT content but the TNT set points essentially remained below 80°C.

The second phase of investigation was the purification of crude TNT using $MgSO_3$. $MgSO_3$ was found to be very effective in removing the TNT meta isomers and producing TNT which satisfied all the requirements of government specification MIL-T-248C. Because of the limited solubility of $MgSO_3$, a recycle process was evaluated to maintain high sulfite concentrations in the purification reaction. The red water produced during purification was easily concentrated and incinerated with a carbon source, to produce MgO. The recovered MgO was reacted with SO_2 to produce $MgSO_3$ which was successfully used to purify crude TNT. Various purification parameters investigated gave the following results:

1. The effect of $MgSO_4$ concentration on the set point of TNT. The maximum concentration which allowed acceptable set points was approximately six percent at a TNT to $MgSO_3$ mole ratio of 14:1 and ten percent at a mole ratio of 10:1.

2. The effect of the mole ratio of TNT to $MgSO_3$. The maximum ratio was 14:1 with a 10:1 ratio being the most acceptable.

3. The effect of contact time between the molten TNT and $MgSO_3$. Approximately 15-22 minutes of contact time are required to produce a consistently acceptable product.

4. The effect of the mole ratio of water to TNT. Most of the runs were conducted at a ratio of 70:1(89:11 volume percent) but a ratio as low as 28:1 (77:23 volume percent) is acceptable.

5. The effect of the refortification of red water with $MgSO_3$. The red water from one run was refortified six times and the resultant TNT acceptable.

RECOMMENDATIONS

1. No further work should be performed at the present time on the use of $(NH_4)_2SO_3$ to purify crude TNT.
2. The comparative cost data reported in June 1979 under, "Task I - Comparative Cost Study of Purification Methods," Production Engineering Report 556 indicates that the $MgSO_3$ process is economically competitive with the Sellite process. However, an evaluation of the full-scale purification or recovery process has not been demonstrated as has been done with the Sonoco Sellite recovery process.

   Therefore, it is recommended that only limited pilot plant efforts be considered on the $MgSO_3$ process since evaluation of scaled up magnesium sulfite systems would be cost prohibitive and occur at a time the Sellite recovery process was well underway.

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