Treating Colored Water in Western North Dakota

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This report is a study made in southwestern North Dakota to determine methods of removing organic coloring and minerals from ground water used for domestic purposes.

Procedures

Eleven rural cooperators with water quality problems were selected for this study. Two were in the Dickinson area and nine in the Hettinger area. These cooperators had worked or consulted with North Dakota State University personnel on previous water related projects. These waters, based on previous observation, varied considerably in color and other properties. The color range of these waters is shown in Figure 1.

Work upon which this project is based was supported by North Dakota Agricultural Experiment Station Project H-4-24.

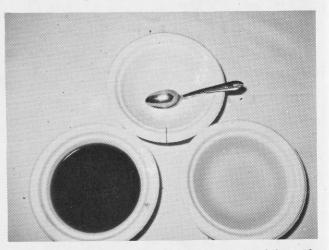


Figure 1. The color of the ground water ranged from the dark sample in lower left to the clear water in upper center.

Water Collection

Forty-gallon samples were collected in plastic water containers from each cooperator's ground water supply. Tests were made in a mobile laboratory located at the Branch Experiment Stations at Dickinson and Hettinger, North Dakota.

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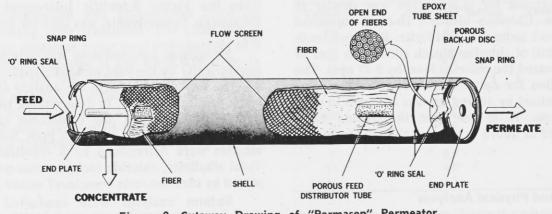


Figure 2. Cutaway Drawing of "Permasep" Permeator. (Courtesy of E. I. Du Pont De Nemours and Company).

Water Treatment Methods

Reverse Osmosis

E. I. Du Pont De Nemours and Company, Wilmington, Delaware, loaned a reverse osmosis unit, Model B-9 "Permasep" permeator, to the Department of Agricultural Engineering for this study. The membrane in this permeator consisted of small (84 microns) hollow nylon fibers about the thickness of a human hair. The hollow fibers are illustrated in Figure 2.

The feed water under pressure flows through the perforated tube inside the permeator bundle and around the fibers. Here, part of the water which later flows out the permeate ports may enter the hollow fibers. The water remaining produces a concentrated brine which flows across the permeator membrane picking up and carrying off unpermeated molecules as it flows to the concentrate port.

The manufacturer's specifications require that the water be pretreated by acidification to pH 5.6 before using reverse osmosis if the calcium ion concentration exceeds 5 ppm. Acidifying the water keeps the calcium compounds soluble and prevents scaling or fouling of the permeator membrane. The calcium ions may also be removed by a resin-exchange water softener.

The calcium ion concentration was determined by analyzing the water for calcium hardness, parts per million (ppm) as calcium carbonate. This calcium hardness level was multiplied by 40 per cent to approximate the calcium ion concentration. The reverse osmosis system was assembled as illustrated in Figure 3.

A submersible pump was used to develop pressure head for the reverse osmosis treatment. A water filter installed ahead of the permeator prevented particles larger than 10 microns from entering the system.

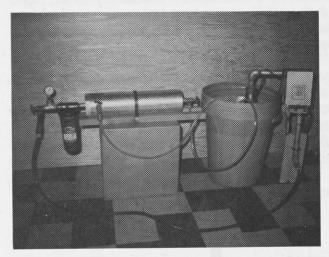


Figure 3. Permeator, Pump and Water Filter assembled for "Water Treatment.

Coagulation

The alum (aluminum sulfate) was acquired from a municipal water plant. The concentration required for optimum removal of color was determined by adding various amounts. One-tenth gram aluminum sulfate (containing 17 per cent water soluble aluminum oxide) was added to each liter of water. This was equivalent to adding 17 ppm as aluminum oxide.

After the chemical was added, each jar was capped with a rubber stopper and inverted four times to disperse the chemical throughout the liquid. This also helped to dissolve the aluminum sulfate since it was added in crystalline form. The alum produced a precipitated floc resulting in a clarified water. The samples were allowed to settle for one hour and then the supernatant was siphoned off. The supernatant flowed directly into a combination sand and carbon filter for further removal of floc.

Chlorination

The process for chlorination was similar to coagulation. Chlorine bleach ("Hi-lex") contained 5.25 per cent sodium hypochlorite. Each one-tenth milliliter (ml) of chlorine bleach added to a liter of water increased the chlorine level by 2.47 ppm. The concentration for optimum oxidation of the color was determined by adding various amounts to each water sample. After one hour, the treated water was filtered as above to remove chlorine taste and odor.

Chemical and Physical Analyses

A "Hach" field test kit, model DR-EL-CM-B, from the Hach Chemical Company, Ames, Iowa, contained a colorimeter, conductivity meter, standard solutions and powder pillows needed for water analyses. This kit was used for all tests unless otherwise stated.

The color level of water, measured in units, platinum cobalt scale, was determined with a colorimeter which was standardized with distilled water. Conductivity was easily and quickly determined by calibrating the meter and immersing the conductivity cell in the sample being measured by selecting the appropriate scale. A "Fisher" accumet pH meter, model 210, from the Fisher Scientific Instrument Division, Pittsburgh, Pennsylvania, was used for determining pH.

Manganese concentration was determined colorimetrically by the cold periodate oxidation method. The field test kit could not analyze manganese levels less than 1 ppm. In determining the amount of iron concentration, the equipment used could not measure less than one-tenth ppm. Sulfates and nitrates were determined by a colorimetric test. Total alkalinity, chloride and hardness were determined by titration tests.

Sodium analyses were conducted on five ground waters and five permeate waters by Lake Agassiz Testing Laboratories, Moorhead, Minnesota. Also, these same samples were analyzed for fluorides using the Hach tester.

The analyses used to show the effects of water treatment on the properties of the ground water consisted of an analysis of ground water, permeated water, coagulated water and chlorinated water. The analysis for the samples selected from a coagulated or chlorinated sample was the one that had the least color after filtration. If two samples contained the same color level, the one which required the least chemical was selected.

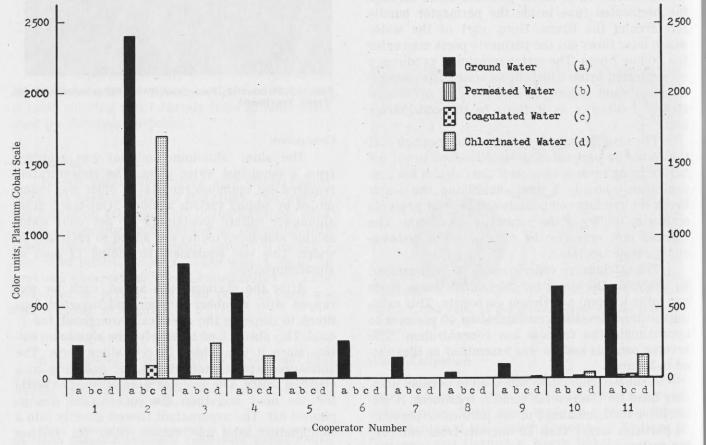


Figure 4. Effects of Water Treatment on Color

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Results

The coagulation and chlorination tests required filtering after treatment. The filter was a large plastic container using sand and charcoal as a filter medium. The size of the filter was large in proportion to the size of the sample. Some of the tests were affected by either the previous sample or by the wash water used to rinse the filter. The reverse osmosis (permeated water) tests were not filtered and therefore were not affected by the filter.

Effects of Water Treatment

Color

The color of these ground waters ranged from 49 to 2,400 color units and was reduced by all treatment methods as shown by Figure 4. The permeator reduced the color to a level below the 15 color units specified by the U.S. Dept. of Health, Education and Welfare Drinking Water Standards. Coagulation was as effective as reverse osmosis for color removal except for two waters. Chlorination did not remove sufficient color when the sample contained about 300 or more color units.

The amounts of aluminum sulfate and chlorine bleach required to produce the minimum color levels for coagulated and chlorinated waters re-

Table	1.	Aluminum	Sulfate	and	Chlorine	Bleach	Dosages
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Cooperator	Aluminum	Sulfate	Chlorine Bleach
No.	g/l		ml/l
1	0.5		0.2
2	4.5		3.2
3	1.5		20.0
4	0.5		20.0
5	0.1		0.2
6	0.5		0.2
7	0.5		0.2
8	0.5		0.2
9	0.5		0.8
10	4.5		3.2
11	1.1		0.8

spectively, are shown in Figure 4 and given in Table 1. Amount of coagulant added ranged from onetenth gram to four-and-one-half grams per liter sample. Excess coagulant produces turbidity which causes apparent color. The chlorine bleach added ranged from two-tenths to 20 ml. per liter sample. Five-tenths ml. per liter chlorine bleach of 12.35 ppm chlorine or more produced a pungent taste and odor in the water and would have required additional treatment for taste and odor removal. Adding more than five-tenths ml. chlorine bleach per liter sample did not seem to be effective in reducing color to a satisfactory level of 15 color units.

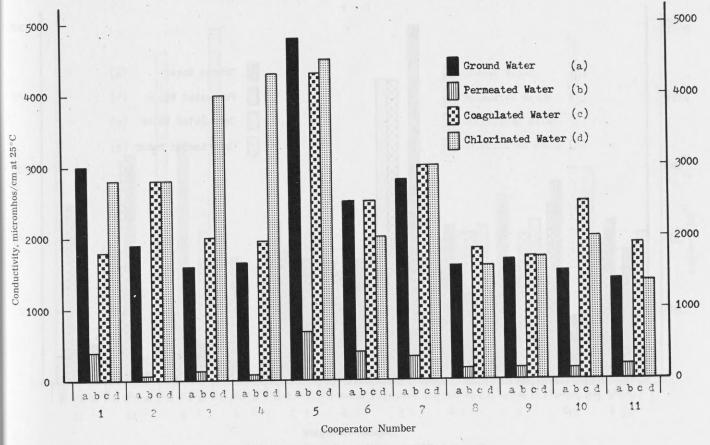


Figure 5. Effects of Water Treatment on Conductivity

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Conductivity

These ground waters are highly mineralized since the conductivity range, 1,400 to 4,800 micromhos/centimeter (cm) as shown in Figure 5 is over 500 micromhos/cm. Waters with over 500 micromhos/cm are highly mineralized.

Reverse osmosis greatly reduced conductivity of all ground waters. Ions that are good conductors such as sodium, chloride and others have an affinity for water and are not removed by coagulation and chlorination treatments. Therefore, the conductivity level should remain the same or increase after coagulation or chlorination, which it did in most cases.

Temperature and pH

The pH of these ground waters was alkaline ranging from pH 7.9 to pH 8.8 as shown in Table 2.

The reverse osmosis process generally reduced the pH of water. Hydroxyl ions may have been removed to lower the pH. Coagulation lowered the pH since aluminum sulfate has an acidic reaction. Most waters coagulated above pH 6. An alkaline reaction is normal for hypochlorites and the pH was reduced. for most samples.

The temperature of the samples is given in Table 2 since pH and conductivity are temperature dependent.

Table 2. Hydrogen ion concentration and temperature of the ground and treated samples.

Ground Water			Permeated Water		Coagulated Water		Chlorinated Water	
Cooperator	Hydrogen ion concentration	Temperature						
No.	pH at 25°C	°C						
1	8.2	10	5.3	18	7.3	14	7.3	22
2	8.0	20	6.8	15	5.8	26	8.6	26
3	8.3	18	6.9	15	6.7	22	8.8	12
4	8.2	26	8.2	26	5.4	26	8.8	26
5	7.9	28	6.9	28	7.1	28	7.2	28
6	8.1	25	6.9	25	7.1	25	7.5	25
7	8.3	33	6.2	32	7.7	33	7.4	33
8	8.7	31	7.0	31	7.9	31	7.6	31
9	8.2	27	7.0	27	7.8	27	7.6	27
10	8.8	27	7.7	27	6.3	27	8.5	27
11	8.4	26	6.9	26	4.9	25	7.4	25

Iron and Manganese

Iron levels ranged from 0.6 ppm to 1.1 ppm as shown in Table 3 for the ground waters. Table 3 shows less than 1 ppm manganese for all waters except a coagulated sample from cooperator 10. Color interfered with analyses for both iron and

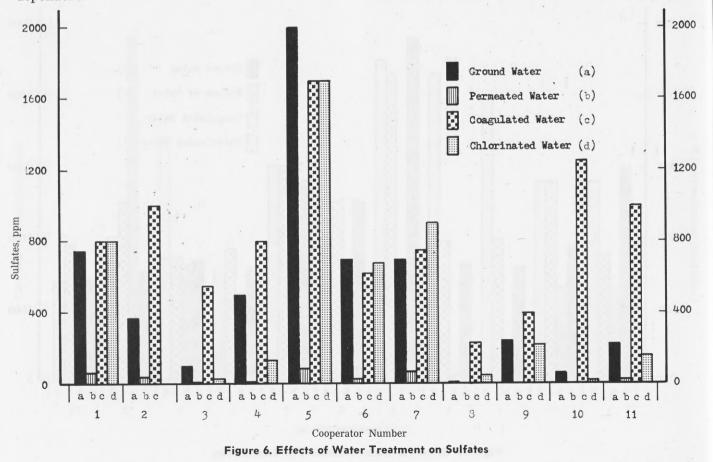


Table 3. Effects of water treatment on iron and manganese

ada"	Serve	Iron			Manganese			
Cooperator	Ground Water	Permeated Water	Coagulated Water	Chlorinated Water	Ground Water	Permeated Water	Coagulated Water	Chlorinated Water
No.	p	arts pe	r millio	on	pa	rts pe	r millio	n
1	0	0	0	0	*	*	*	*
2	- 0	0.1	1.3	0	*	*	*	*
3	0.9	0	0	1.0	*	*	*	*
4	1.1	0	0	0.7	*	*	*	*
5	0.9	0	0	0	*	*	*	*
6	0.6	0	. 0	0	*	*	*	*
7	0	0	0	0	*	+		
8 .	0	0	0	.0.	*	*		
9	0	0	0	0	*			
10	0	0	0.1	0	*	*	1.3	
11	0	0	0.3	0.2	*	*		

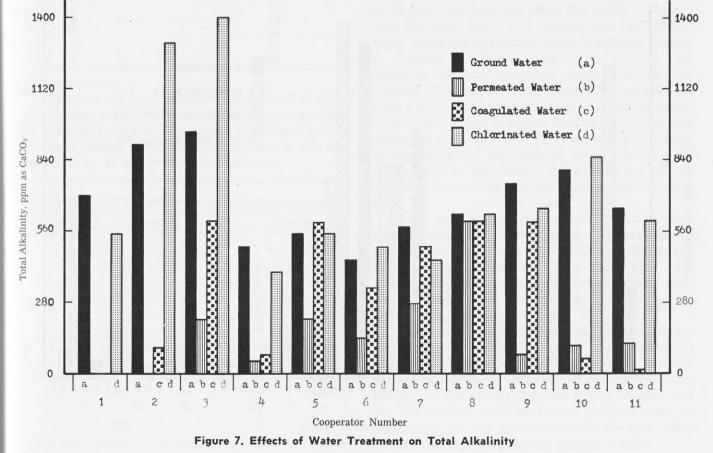
manganese because levels of these minerals detected in the clarified water were sometimes greater than those in the ground water. The coagulated samples from cooperators 2 and 10 would have created staining problems on fabrics due to iron levels above 0.3 ppm and manganese above 0.05 ppm, respectively. Iron in the chlorinated samples from cooperators 3 and 4 would also have created staining problems. The test procedures did not permit determination as to whether other treated waters in Table 3 would have had a staining effect.

Sulfates

One-half the ground waters in Figure 6 contained sulfate levels in excess of the 250 ppm recommended by Drinking Water Standards. The permeator reduced the sulfate levels satisfactorily. Lower sulfate levels were measured in two waters after coagulation and in six samples after chlorination. Again, the color in the water may have interfered with these tests. Sulfates in the coagulant (aluminum sulfate) increased the sulfate level in most waters treated by coagulation. No change in sulfate level by chlorination was expected and variations in results were probably due to contamination from the large filter.

Nitrates

The nitrate levels for the ground waters were well below the 45 ppm recommended by Drinking Water Standards. The two permeated waters that were analyzed for nitrate content showed reverse osmosis did reduce the nitrate level (Table 4).



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Table 4.	Effects	of the	permeator	on	nitrates.
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Cooperator	Ground Water	Permeated Wa	ter
No.*	ppm	ppm	
1	12	0	
4	4	**	
11	5	2	

Alkalinity

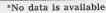
The ground waters tested were quite alkaline as shown in Figure 7. The total alkalinity ranged from 450 ppm to 950 ppm. These alkalinity levels were reduced by reverse osmosis. The alkalinity increased after coagulation of water from cooperator 5. Effects caused by contamination during filtration were likely the reason for this upward trend because aluminum sulfate destroys alkalinity. The alkalinity increase in samples from cooperators 2, 3 and 10 after chlorination may have been due to chlorine's alkaline reaction with water.

Chlorides

These ground waters contained chloride levels below the 250 ppm recommended by Drinking Water Standards. Chlorides ranged from 10 ppm to 75 ppm as shown in Table 5. The permeator reduced the chloride levels of most waters except for cooperator 10 which remained the same. The changes in chloride levels in the coagulated water was probably due to contamination effect in the filter. Chlorination raised the chloride levels in the natural waters.

Table	5.	Effects	of	water	treatment	on	chlorides.	

Cooperator	Ground Water	Permeated Water	Coagulated Water	Chlorinated Water
No.	ppm	ppm	ppm	ppm
1	15	.5	*	- 45
2	*	*	20	2000
3	20	5	100	. 1125
4	50	5	25	950
5	12	7	30	30
6	35	7	55	40
7	10	10	30	35
8	75	10	. 70	90
9	20	10	25	50
10	· 15	15	20	140
11	30	10	20	50



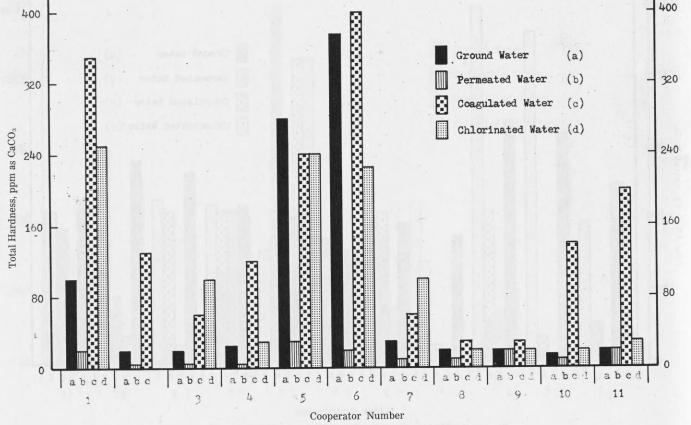


Figure 8. Effects of Water Treatment on Total Hardness

Total Hardness

Most of the ground waters tested were soft, but three samples contained 100 ppm to 375 ppm total hardness as shown in Figure 8. The permeator softened all waters except samples from cooperators 9 and 11 which retained their 20 ppm hardness. In the coagulated method the aluminum ions in the coagulant increased the hardness of waters from all cooperators except 5. The chlorinated water was not affected, because chlorine bleach does not contain hardness producing ions. Therefore, contaminating effects during filtration obviously hardened the chlorinated samples of water from cooperators 1, 3, 7 and 11. The aluminum ions from the coagulant or the hardness producing compounds from the water used for backwashing the filter may have affected the water hardness of these samples.

Table	6.	Calcium	hardness.
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Cooperator	Ground Water
No.	ppm
1	70
· 2	10
3	10
4	10
5	150
6	200
7	10
8	10
9	10
10	10
11	10

Calcium Hardness

Range of calcium hardness was from 10 to 200 ppm as shown in Table 6 with many of them having the minimum amount. The degree of calcium hardness is important because of its effect on the life of the cartridge in the reverse osmosis unit.

Table 7. Effects of the permeator on sodium and fluori
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Cooperator	So	dium	Fluoride		
•	Ground Water	Permeated Water	Ground Water	Permeated Water	
No.*	parts per	r million	parts p	er million	
7	360	80	4.5	0.7	
8.	295	37	4.1	0.6	
9	308	38	5.5	0.6	
10	352	70	6.5	0.9	
11	315	72	7.0	1.4	

*No data is available for cooperators no. 1 through 6.

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Sodium and fluoride levels in Table 7 for ground waters ranged from 295 ppm to 360 ppm and 4.1 ppm to 7.1 ppm, respectively. These minerals were significantly reduced by reverse osmosis. Color interference may have produced high readings for fluorides in the ground water samples.

Conclusions

Reverse osmosis worked very effectively when treating colored ground waters. This method produced water from all samples treated that met U. S. Department of Health, Education and Welfare Drinking Water Standards. Large amounts of color were removed by the reverse osmosis process. This treatment method also reduced the levels of conductivity, sulfates, alkalinity, chlorides, hardness, fluorides, sodium and possibly iron found in these waters. Another good feature of reverse osmosis is that usually no chemicals had to be added to the water. The exception was that water needs to be acidified if it contains high calcium ion concentrations.

The analysis of the coagulated and chlorinated waters did not always meet Drinking Water Standards following filtration. The coagulant (aluminum sulfate) removed color effectively from all but two waters in this investigation. Chlorination (chlorine bleach) did not reduce color to an acceptable level of 15 color units or less when the water contained over 300 color units. It is obvious that the conductivity generally increased when aluminum sulfate or chlorine bleach was added to the sample. This indicates the total dissolved solids were also increased. The coagulant contained water soluble sulfates which obviously increased the sulfate levels when it was added to water. Aluminum sulfate also hardened water when used as a coagulant. Chlorination increased the chloride levels. Sulfates, nitrates, sodium, chlorides and fluorides are not expected to be removed by coagulation and chlorination.

Iron and manganese removal from colored ground waters by reverse osmosis, coagulation and chlorination can not be truly evaluated due to the limitations of the tests used. Less than 1 ppm manganese was not measurable with the "Hach" field test kit. Also, color interfered with these tests as well as other colorimetric tests.

Obviously, results from coagulated and chlorinated samples were affected by contaminants in the large sand and activated carbon filter. A smaller filter would have given better results. The comparison of the results between the permeator and the coagulated and chlorinated samples were so conclusive that any errors caused by the large filter did not materially affect the general results.