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Detergent Considerations for Consumers: Laundering in Hard Water—How Much Extra Detergent Is Required?

Bruce A. Cameron

Associate Professor, Textiles and Merchandising
University of Wyoming
Laramie, Wyoming
unsw@uwyo.edu

Abstract: Laundering is a complex process, and detergents have changed considerably over the last 20 years. The research reported will be of benefit to both Extension educators and teachers in advising people with whom they work on choices between different types of laundry detergents when it comes to laundering. Liquid detergents washed equally well in both soft and hard water. Powdered detergents were better than liquids in soft water. Water hardness affected powdered detergents, and, depending on the detergent type, 10-15% to > 30% extra detergent was needed to obtain a result similar to that of soft water.

Introduction

Laundering is a complex process. It is not uncommon to try detergent after detergent until the one that functions the best under the different conditions of water used or soils to be removed is found (Spirit of Research, 1966). The formulations of laundry detergents are varied, with ingredients designed to perform broad cleaning functions and to provide properties specific to a product (American Cleaning Institute (ACI), 2010a). Detergents are considered to be either general purpose (suitable for all fabric types) or light duty (suitable for lightly soiled and delicate fabrics) (ACI, 2010a). No matter the detergent, water conditions have the potential to affect the cleaning process.

Laundry detergents may contain any number of ingredients designed to enhance the laundry process. However, there are typically two major ingredients, a surfactant and a builder. The surfactants (surface active agents) loosen and remove soil, emulsify, or suspend soils in the wash, and improve the wetting ability of water (Ainsworth, 1994). Builders reduce water hardness (Kirschner, 1998) by combining with divalent calcium and magnesium ions, making them less available and thus prohibit their interference with the surfactant action (Rutkowski, 1981). Examples of builders used in laundry powders include sodium tripolyphosphate, sodium carbonate, sodium citrate, and zeolites (Kirschner, 1998). Detergents built with phosphates performed better than detergents built with other compounds (Cameron & Brown, 1995). However, phosphate builders are rarely used in the U.S. (McCoy, 2000), because they have been blamed for causing eutrophication (high concentrations of nitrates and phosphates which causes excessive algae growth) of lakes and other bodies of water.

Water quality is often overlooked in the laundering process. From a laundering perspective, the most important factor is the presence of calcium and magnesium compounds. These minerals make the water "hard" (Heidekamp & Lemley, 2005). Depending on the concentration of calcium and magnesium present in the water, hard water can be classified as moderately hard, hard, or very hard. Water hardness is measured in grains per gallon (gpg) or parts per million (ppm). The American Society of Agricultural Engineers (ASAE) water classification table is shown in Table 1 (Manikowske, 1994). A large proportion of the United States has hard water. Figure 1 shows the water hardness throughout the United States as determined by the U. S. Geological Survey (USGS). This figure shows that about 85% of the United States has water hardness problems (USGS, 2009). While the map shows water hardness data from 1975, "these data have been found to be accurate and useful in current assessments" (USGS, 2009, p1).

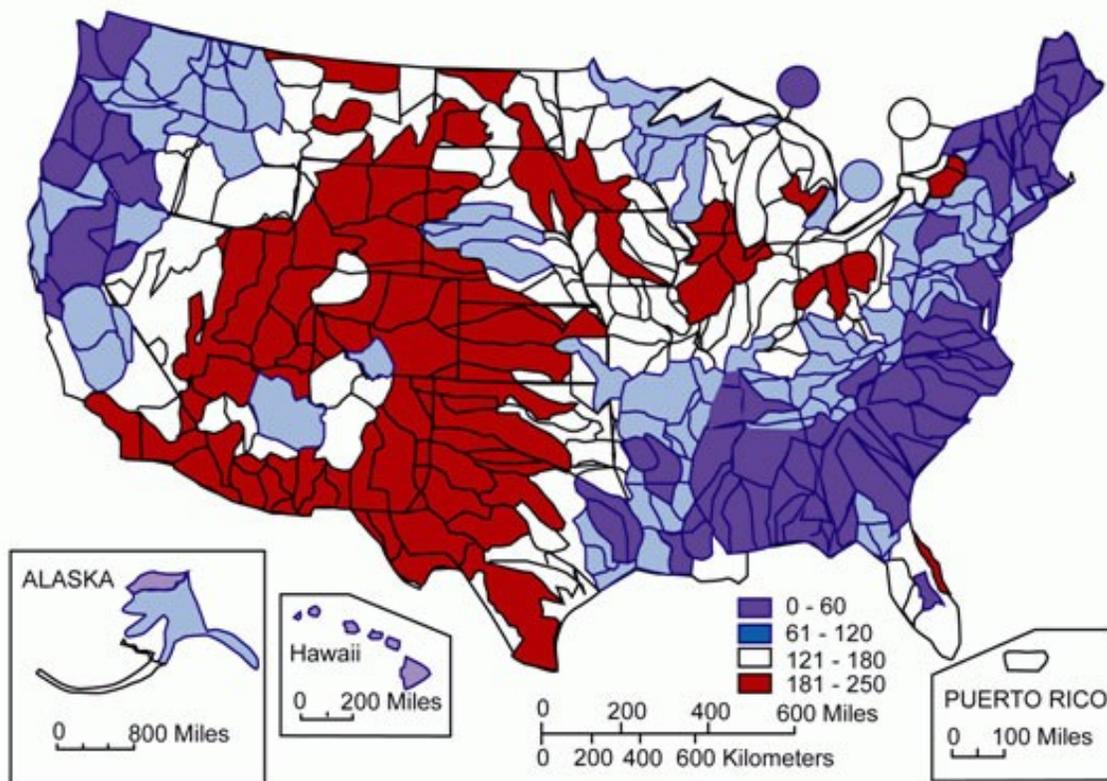
Table 1.
ASAE Water Hardness Classification

	Grains per Gallon	Parts per Million
Soft	0 to 3.5	0 to 60
Moderate	3.6 to 7	62 to 120
Hard	7.7 to 10.5	121 to 180
Very Hard	More than 10.5	More than 180

Water hardness causes mineral buildup on appliances (washing machine), decreasing the life of these appliances (Wilson, 2009), and reduces the efficiency of detergents (Stone, 2009). These mineral deposits can cause clothes to appear dingy and become harsh and scratchy to touch (Heidekamp & Lemly, 2005; Vanderpoorten Beard, 1999; Hairston & LaPrade, 1995). Continuous washing in hard water can cause significant damage to fibers and shorten the life of a fabric due to edge abrasion (Munson, 1991).

Figure 1.
Map of Water Hardness Found in the United States (USGS, 2009)

**CONCENTRATION OF HARDNESS AS CALCIUM CARBONATE,
IN MILLIGRAMS PER LITER**



Laundry powders were the dominant consumer choice in the early 1990s, accounting for about 60% of detergents used (Morse, 1999). By the mid 1990s, the market was nearing a 50-50 split between powders and liquids (Kirschner, 1998), primarily because liquids were easier to use and dissolved better in hard water. By 2004, liquid laundry sales accounted for 75% of the market, with sales of more than \$2.4 billion (McArdle, 2005). Sales of liquid detergents have only continued to increase. In 2009, liquid detergents accounted for 83% of the market, with sales of \$3.1 billion (McCoy, 2010).

The purpose of the project reported in this article was to evaluate the effectiveness of 14 consumer laundry detergents, six powders and eight liquids, in terms of how effectively they cleaned a standard soiled cloth in soft water (deionized water) and water of 100 ppm hardness. In addition, if the samples washed in the hard water were significantly different from those washed in the soft water, the research sought to determine how much extra detergent was required when washing in the hard water to bring the cleanliness to those comparable with the soft water.

Materials and Methods

Fabric

A 65/35 polyester/cotton standard soiled standard fabric (EMPA-104, 58", 147 g/m²) was purchased from Testfabrics Incorporated, West Pittston, PA. The standard soil, covering the entire fabric, consisted of carbon black/olive oil. A 65/35 polyester/cotton blend was chosen for the research as it represents the most common

blend type used in textile applications (Advertising Specialty Institute, 2006). Fabric samples were cut to 150mm x 125mm (6" x 5"). These samples weighed 3.1 ± 0.05 g.

Detergents

Fourteen detergents (purchased from a local supermarket) contained the ingredients as listed on the packaging are shown in Table 2. Eight liquid detergents (two containing a bleach alternative) and six powdered detergents (one containing a bleach additive) were purchased.

Table 2.
Detergent Formulations

Detergent #	Type	Formulation
1	Powder	Biodegradable anionic and/or nonionic surfactants, water softeners, brightener, perfume, processing aids
2	Powder	Biodegradable surfactants and enzymes
3	Liquid	Biodegradable surfactants (anionic and nonionic) and enzymes. Contains bleach alternative
4	Liquid	Biodegradable surfactants (anionic and nonionic) and enzymes
5	Liquid	Biodegradable surfactants (anionic and nonionic)
6	Liquid	Biodegradable surfactants (anionic and nonionic) and enzymes
7	Liquid	Biodegradable surfactants (anionic and nonionic), enzymes, baking soda, perfume
8	Liquid	Biodegradable surfactants (anionic and nonionic) and enzymes
9	Liquid	Cleaning agents (biodegradable surfactants), fragrance and colorant. Contains bleach alternative
10	Liquid	Biodegradable surfactants (anionic and nonionic) and enzymes
11	Powder	Biodegradable anionic surfactants and enzymes
12	Powder	Biodegradable anionic surfactants and enzymes
13	Powder	Biodegradable surfactants and enzymes. Contains bleach additive
14	Powder	Anionic and nonionic surfactants, sodium carbonate and enzymes

Water

Deionized water was prepared according to the method described by Cameron (2007). Water of 100 ppm hardness was prepared by dissolving 2 ± 0.001 grams of calcium carbonate in a minimum of dilute hydrochloric acid (5% solution) and then neutralized with a dilute sodium hydroxide solution (5%) until slightly alkaline to litmus. One gram of calcium carbonate dissolved in one liter of water makes a 1000 ppm solution. The resulting solution was then diluted to 20 liters with deionized water to produce water of 100 ppm hardness. A water hardness of 100 ppm was chosen for the study because a previous study (Kushner & Hoffman, 1951) found that to clean as effectively in water of 100 ppm hardness compared to that of distilled water, 10% more soap was required. The hardness of water samples prepared was tested according to the method of Schwarzenbach (Milwidsky & Gabriel, 1982).

Wash Solutions

Solutions of detergents were made up a 0.5% weight/volume (w/v) dilution (Cameron & Brown, 1995; Cameron 2007). This was achieved by dissolving 3.00 ± 0.005 g of detergent in 600ml of either deionized water or 100 ppm hard water. These detergent solutions would be more concentrated than those normally used in domestic washing machines, meaning more surfactant was available for cleaning.

To evaluate how much extra detergent was required when washing in the 100 ppm hardness water to bring the cleanliness to those comparable with the soft water, wash solutions for the powdered detergents were also made by dissolving 3.25 ± 0.005 g (0.542% w/v), 3.50 ± 0.005 g (0.583% w/v) and 3.75 ± 0.005 g (0.625% w/v) in 600ml of water. These solutions were 8.3%, 16.7% and 25% more concentrated respectively.

Laundering

Laundering tests for detergency analysis were carried out using a launder-ometer (Atlas Electric Devices Co.). Washing tests were performed for 15 minutes at a temperature of 30°C (86°F). Many laundering tests typically call for the use of a standard washing machine. The launder-ometer was chosen for these tests because it provides for an accelerated procedure because agitation is continuous, whereas in standard washing machines the agitation is intermittent (Cameron, 2007).

Five samples were washed individually each in 100ml of wash solution for each of the 14 different detergents. After washing, samples were rinsed in cold running water and hung to air dry.

Measurement of Whiteness Indices

Whiteness indices were determined according to Cameron (2007) using a reflectance colorimeter (Color Sphere — Byk Gardner). The whiteness indices were used as a measure of how clean samples were; the higher the whiteness index, the cleaner the sample.

Statistical Analyses

The significance of the effectiveness of the detergents in cleaning samples as evidenced by change in whiteness was determined using *t* tests. Ordinary least-squares (OLS) regressions were used to further examine the relationship between powdered detergent concentration and whiteness indices. Anova's were used to determine the significance of linear regressions. The level of significance for all statistical tests was $p < 0.05$.

Results and Discussion

Table 3 shows the whiteness indices for the standard soiled fabric using the various detergents in the soft and water of 100 ppm hardness. The results indicate that the liquid detergents were not affected by the increase of the water hardness (no significant difference); however, the powdered detergents were affected. Whiteness indices for the powdered detergents were significantly lower in the 100 ppm hardness water compared to that of the soft water. However, in soft water, the powdered detergents performed significantly better than any of the liquid detergents.

Table 3.

Whiteness Indices (Mean and Standard Deviation) of 14 Consumer Laundry Detergents in Deionized (Soft) Water and Water of 100 ppm Hardness; 0.5% w/v

Detergent	Soft Water		100 ppm Water	
	Mean	SD	Mean	SD
1	20.17*	2.59	15.90* ^a	1.99
2	23.90*	2.67	19.12* ^a	2.28
3	15.84*	1.47	16.32*	4.02
4	11.55*	1.17	12.14*	1.92
5	11.83*	2.45	12.19*	2.43
6	12.20*	1.28	12.06*	2.28
7	12.40*	1.81	12.44*	3.06
8	11.70*	1.19	12.53*	2.71
9	16.43*	2.58	17.49*	2.58
10	14.55*	1.75	15.59*	2.80
11	19.86*	2.78	13.87* ^a	2.23
12	22.48*	2.90	17.49* ^a	3.56
13	28.50*	3.62	24.11* ^a	2.79
14	20.32*	2.98	16.28* ^a	2.62

Note: Whiteness Index Control (soiled test fabric) = 5.29
 * Significantly different ($p < .05$) than control
 a. Significantly different ($p < .05$) from deionized water wash

Liquid laundry detergents perform equally well in both soft and hard water, thus if consumers are concerned about water hardness, the use of liquid detergents would most likely be the best choice. This is due to the fact that liquid detergents contain nonionic surfactants. These surfactants do not ionize in solution and so have no electrical charge (ACI, 2010b). As such, they are resistant to water hardness (ACI, 2010b) and, because they contain no ionic groups, dissolve equally well in a variety of temperature and water hardness conditions

(Cameron, 2007; Cameron & Brown, 1995). Nonionic surfactants, because they have no charge associated with them will not precipitate out of solution and cause a scum.

Table 3 shows that in water of 100 ppm hardness the whiteness indices for powdered detergents were significantly lower than those obtained in soft water. In the water of 100 ppm hardness, many powders still out performed liquids (gave whiteness indices higher than those of liquid detergents). However, the problem with using powders in hard water situations is that they typically contain anionic surfactants. These surfactants ionize in solution and carry a negative charge (ACI, 2010b). This negative charge enables these surfactants to combine with the divalent calcium ions in the hard water to form a scum that is not water soluble. This mineral buildup can decrease the life of appliances (Wilson, 2009), reduce the efficiency of the detergent (ACI, 2010c; Stone, 2009), and cause clothes to appear dingy and become harsh and scratchy to touch (Heidekamp & Lemly, 2005; Vanderpoorten Beard, 1999; Hairston & LaPrade, 1995).

Table 4 shows the results of washing in soft water and 100 ppm hardness water (with different concentrations of detergents) for the six powdered detergents. It appears that in all cases, the whiteness indices are increasing somewhat linearly when washing in 100 ppm hardness water.

Table 4.

Whiteness Indices (Mean and Standard Deviation) of 6 Consumer Powdered Laundry Detergents in Deionized (Soft) Water and 100 ppm Hardness Water at Different Concentrations

Detergent	Soft Water		100 ppm Water					
			Detergent Concentration					
	Mean	SD	0.542% w/v		0.583% w/v		0.625% w/v	
Mean			SD	Mean	SD	Mean	SD	
1	20.17*	2.59	18.79*	3.35	21.30*	2.74	24.60* ^b	3.32
2	23.90*	2.67	21.33* ^a	3.16	24.77*	2.37	28.41* ^b	3.48
11	19.86*	2.99	16.30* ^a	2.93	18.35* ^a	3.66	20.36*	3.16
12	22.48*	2.90	18.75* ^a	3.82	20.42* ^a	3.09	21.86*	2.65
13	28.50*	3.62	26.22* ^a	3.41	30.35* ^b	3.26	33.22* ^b	2.79
14	20.32*	2.98	17.15* ^a	4.65	17.78* ^a	3.52	18.93* ^a	2.23

Note: Whiteness Index Control (soiled test fabric) = 5.29
 * Significantly different (p < .05) than control
 a. Significantly different (p < .05) lower whiteness index from deionized water wash
 b. Significantly different (p < .05) higher whiteness index from deionized water wash

Because powdered detergents were affected by water hardness, they were evaluated to determine how much extra detergent was required to achieve results comparable to those achieved in soft water. Model regression equations and R² values for all six powdered detergents can be seen in Table 5. All regression models were significant (p < 0.05) and fit the data well (R² > 0.7).

Table 5.
Regression Equations and R² Values for Powdered Detergents

Detergent	Regression Equation	R ² Value	Detergent Requirement (%)
1	$y = 27.818x + 4.655$	0.807	11.5
2	$y = 33.633x + 4.646$	0.859	14.5
11	$y = 22.227x + 4.831$	0.745	35.2
12	$y = 25.829x + 5.137$	0.799	34.3
13	$y = 42.367x + 4.774$	0.908	12.0
14	$y = 22.003x + 5.247$	0.719	37.0

y = whiteness index
x = detergent concentration (percent w/v)

Based on the regression equations, we can predict for each detergent the concentration that would be required to obtain a whiteness index in hard water equivalent to that in soft water. Using detergents 13 and 14 from Table 5 as examples (these two detergents represented the highest and the lowest R² values—detergent 13 R² = 0.908, detergent 14 R² = 0.719), the concentration for detergent 13 would need to be 0.56% (an increase of about 12%), while the concentration for detergent 14 would need to be 0.685% (an increase of about 37%) to obtain whiteness indices equivalent to that found in soft water. The whiteness indices for detergents 13 and 14 in soft water were 28.50 and 20.32 respectively. Detergents 1 and 2 required between 10-15% extra, while detergents 11 and 12 required >30% extra detergent.

The harder the water, the more difficult the cleaning (Munson, 1991). Kushner and Hoffman (1951) reported that to clean as effectively in water of 100 ppm hardness compared to that of distilled water, 10% more soap would be required. Munson (1991), Mock and Jennings (1996) reported that extra detergent would be required if washing in hard water. The American Cleaning Institute indicates that while detergents are less sensitive to water hardness than soap, they still need help. "Add slightly more detergent than the product label directions recommend" (ACI, 2010c, p1). While additional detergent can certainly be added, the use of powdered detergents in hard water may not be practical from an economic standpoint. The concentration of detergent reported in the research was 0.5%. Using the measuring cups provided with the detergents would have resulted in a detergent concentration of 0.25-0.28%. This would mean that for the detergent requiring the greatest amount of additional detergent reported here; approximately 2½ scoops would be required.

Implications

Water of 100 ppm hardness, soft water (deionized) and detergents were the variables reported in the research. The information provided by the research will be of benefit to both Extension educators and teachers in advising people with whom they work on consumer issues by providing evidence that can help consumers make choices between different types of laundry detergents when it comes to laundering. For Extension educators to be able to help clientele who have questions or concerns relating to laundry problems due to hard water, the following should be taken into account.

- The actual water hardness. Information on water hardness can usually be obtained from the municipal water department. Water hardness test kits can also be purchased.
- The laundry product used and the product ingredients. Information on laundry product ingredients can be found through the American Cleaning Institute (ACI, 2010d). Links are provided to major manufacturers where products can be searched and ingredient lists found. These ingredient lists are much more extensive than that typically found on packaging.
- Liquid detergents perform equally well in all water conditions. Cameron and Brown (1995) found that it wasn't until water hardness reached levels of 750 ppm that liquid detergents were affected.
- Powdered detergents outperform liquid detergents in soft water. This is most likely due to the combinations of surfactants used as well as the fact that the powders are able to dissolve easily in soft water conditions.
- The effectiveness of powdered detergents decreases in hard water. This is due to anionic surfactants combining with the divalent calcium ions in the hard water to form a scum that is not water soluble. This reduces the efficiency of the detergent.
- More than 30% additional detergent may be required to allow powdered detergents to perform as effectively in hard water as they do in soft water. However, this may not be feasible from an economic standpoint as well as the fact that it may be difficult to dissolve this much extra detergent.

Conclusions

The research findings indicated the use of powdered detergents is affected by water conditions. In soft water, powders outperformed liquids and would be the best choice. Liquid laundry detergents perform equally well in both soft and hard water. Overall, of the detergents reported in the research, the powdered detergent that performed the best in both hard water and soft water in terms of whiteness was Detergent 13, a powder with a bleach additive. However, consumers should be aware that the detergent, while providing the highest level of whiteness, could still be problematic in a hard water situation with the likely precipitation of scum. The best performing liquid detergent was Detergent 9.

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