An Improved Method for Evaluating Detergent Builders for Water Hardness Control

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Commercial detergent additives to control water hardness may act through sequestration, crystal growth inhibition, precipitation, or ion exchange. These builders lower the free hardness (Ca^{++}, Mg^{++}) concentration by different mechanisms. A full factorially designed experiment has been developed to evaluate builders functioning by the sequestration or crystal growth inhibition of calcium carbonate or magnesium hydroxide. The builder's performance is determined by its ability to prevent precipitation while in the presence of carbonate and hardness ions. The tests are based on incubation followed by filtration and determination of calcium and magnesium in the filtrate by Inductively Coupled Plasma (ICP). Variables in the design include builder concentration, temperature, pH and time. Regression equations and response surfaces for tripolyphosphate and several polyacrylates and phosphonates are included.

Approximately 25% of the U.S. population cannot purchase a phosphate-based detergent. Holland, Italy, West Germany and Switzerland all have limits on phosphates in detergents. The search for viable environmental and economic alternatives in detergents has continued unabated since the sixties when tripolyphosphates were found to cause environmental problems through eutrophication. These water hardness-controlling agents (detergent builders) are commonly used in synthetic detergents to reduce the free hardness (calcium and magnesium) which in turn is responsible for reduced cleaning.

Water hardness-controlling agents commonly used in the detergent industry are one of three major types (4): (1) sequestrants/threshold inhibitors such as tripolyphosphate, polyacrylates and phosphonates; (2) precipitant builders such as sodium carbonate, and (3) ion exchange builders such as zeolites. Of the three the first is the largest class and the fastest growing. The experimental methods for assessing their value in water hardness control include turbidimetric titrations (2), acidimetric titrations (3) and ion selective electrode titrations (1,4). The first two have been used for over 20 years and, although they are relatively quick, their precision and flexibility are limited. Ion selective electrodes have been used more recently and found to be very useful in comparing detergent builders (including polyacrylates) under similar conditions. Current electrodes, however, do have their limitations. They have limited pH ranges and problems with interfering ions and they require different measurements with two electrodes to differentiate calcium and magnesium (5,6). In addition, since phosphonates are used as electrode solvents, measurement in the presence of phosphonates causes electrode drift. Many unpublished procedures exist for studying scale generation under "realistic" conditions of temperature, salt concentration, etc. (7,8). The use of designed experiments in industry is widespread and well documented (9,10). We report here the relative water hardness control performances of tripolyphosphate as well as several phosphonates and polyacrylates using two 2-level full factorial designed

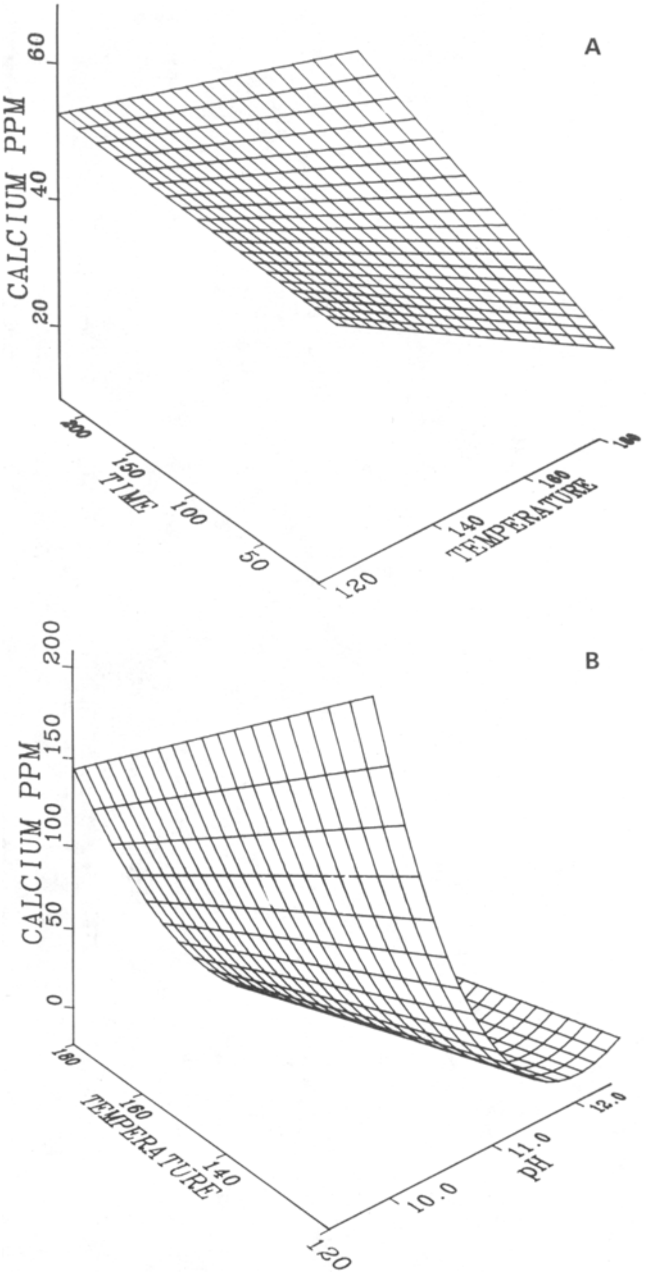

FIG. 1. Perspective plots for calcium in solution in the absence of builder for (A) time and temperature and (B) pH and temperature.

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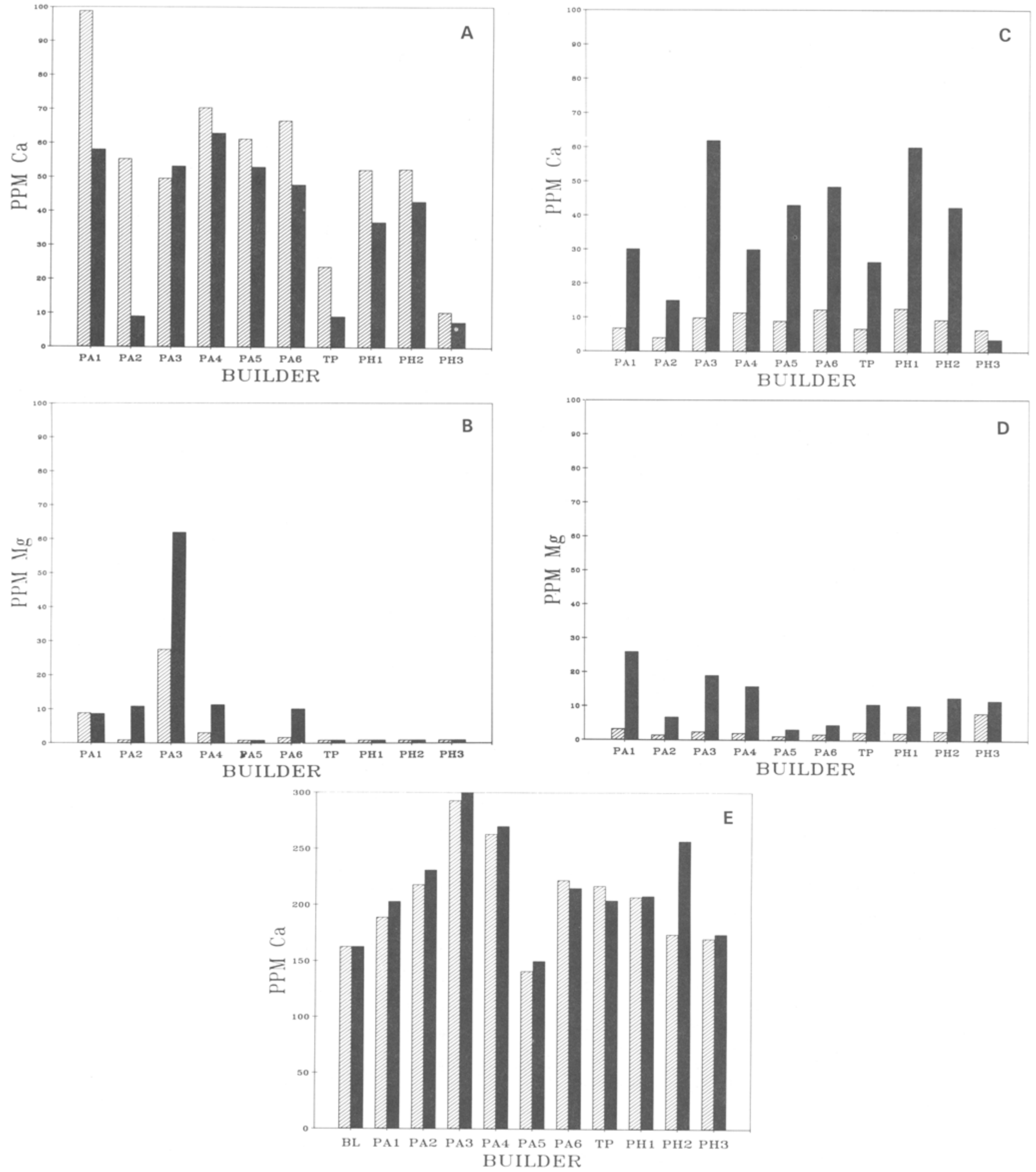

FIG. 2. Comparison of builders ability to keep calcium and magnesium in solution. (A) and (B) pH 12.5, average "effect" of 49 C (120 F) and 82 C (180 F) and 50 and 200 ppm builder. □, 15 min; ■, 225 min; (C) and (D) pH 11, 66 C (150 F), 135 min. □, 15 ppm builder, ■, 125 ppm builder (centerpoints); (E) pH 9.5, average "effect" of 49 C (120 F) and 82 C (180 F) and 15 and 225 min, □, 5/25 ppm avg.; ■,50/200 ppm avg.

experiments. The design's purpose is to create realistic conditions of temperature, time, pH and builder concentration and to develop an understanding of these response surfaces in an efficient fashion. The regression analysis and response surface generation detailed in this work were done on mainframe computers. Several good microcomputer programs have now appeared which can handle the analysis and plots, and these would be highly recommended for the design described herein (11,12).

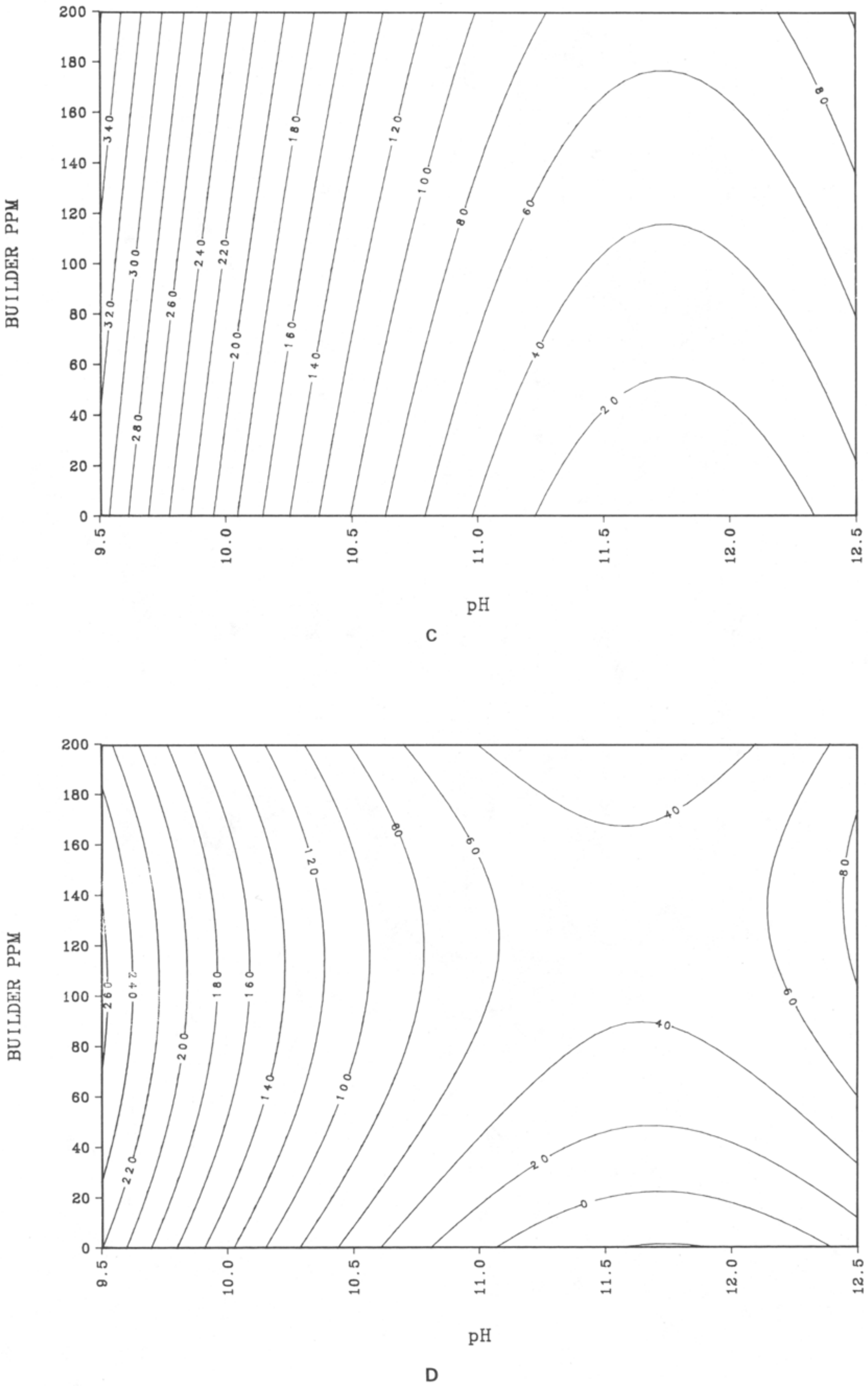

FIG. 3. Response surfaces for calcium in solution (49 C/120 F) as a function of pH and builder concentration for (C) polyacrylate 3, and (D) pohsphonate 2.

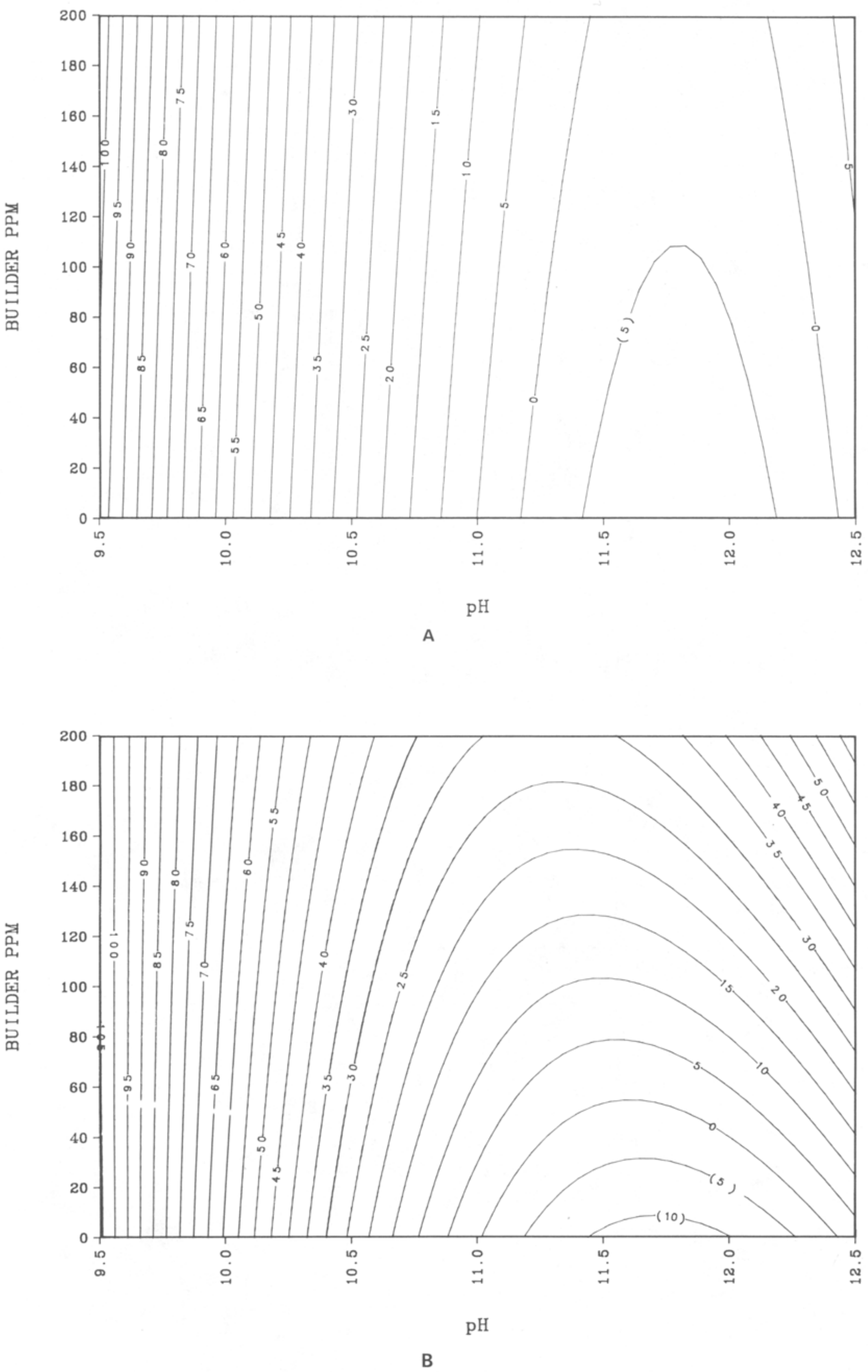

FIG. 4. Response surfaces for magnesium in solution (49 C/120 F) as a function of pH and builder concentration for (A) polyacrylate 4, and (B) polyacrylate 3.

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[Received May 28, 1986]