Recent Developments in the Field of Inorganic Builders

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ABSTRACT

Inorganic builders offer limited choice. Certain sodium aluminum silicates may be used as laundry detergents in combination with sodium triphosphate (STP). Sodium aluminum silicates are available on an industrial scale. They are toxicologically and ecologically safe, and because of their inorganic nature, they do not cause any problems concerning biological degradability; also, they do not contribute to eutrophication. In our experience binary builder systems have proven useful. These consist of STP and the sodium aluminum silicate, in which there is a balance between the chelating ability of STP and the ion exchanging ability of the sodium aluminum silicate. The technical manufacture of laundry detergents on this basis does not present any fundamental problems and does not require technological change.

INTRODUCTION

In the chemical industry, research and development has responded to the worldwide discussion of the eutrophication of surface waters by phosphates by a search for new builder systems. This search turned out to be very difficult, as the technological, toxicological, and ecological properties of new builders have to meet extraordinarily high standards.

ALTERNATIVE INORGANIC BUILDERS

Recently, the focal point has shifted from organic to inorganic builders. In contrast to the greater variety of organic complexing agents and builders, inorganic builder substances are limited to only relatively few types of compounds. They may be classified in two groups with regard to their solubility (Table I).

There is a strong interest in inorganic builders, on the one hand, because of the lack of dependence on mineral oil as the raw material base and, on the other hand, because problems of biodegradability and possible metabolites do not exist.

INORGANIC BUILDERS

Water-soluble Alkalizing Agents

Among the water-soluble inorganic compounds, there are only limited possibilities for the application of sodium carbonate and sodium silicate, as they contribute to the washing performance solely by the electrolyte effect and their alkalizing properties. The desirable ability to complex Ca and Mg ions is lacking.

TABLE I

Inorganic Builders

Water-soluble compounds	Water-insoluble compounds
Sodium carbonate (Na_2CO_3)	Certain Na-Al-silicates ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$) e.g., zeolite A
Na-silicate ($xNa_2O \cdot ySiO_2$)	
Na-diphosphate ($Na_4P_2O_7$)	
Na-triphosphate ($Na_5P_3O_{10}$)	

Water-soluble Complexing Agents

Lower-condensed phosphates, such as tetrasodium diphosphate ($Na_4P_2O_7$) and particularly the most frequently used pentasodium triphosphate ($Na_5P_3O_{10}$) possess properties which are of far greater importance for the washing process. They contribute essentially to washing performance by the following effects:

1. complexing of Ca^{++} and Mg^{++} ions,
2. electrolyte effect and alkalization,
3. specific washing action based on the interaction with solid surfaces.

Thus any reduction of the phosphate content in presently used laundry detergents has a considerable influence on primary and secondary washing performance. Below a certain limiting concentration, there is no free sodium triphosphate (STP) available for soil removal nor sufficient STP for complexing of hardness ions. Massive incrustations caused by the precipitation of calcium and magnesium phosphates are the consequence (Fig. 1).

Water-insoluble Ion Exchangers

Until quite recently, the idea of using water-insoluble builders in laundry detergents has not been seriously pur-

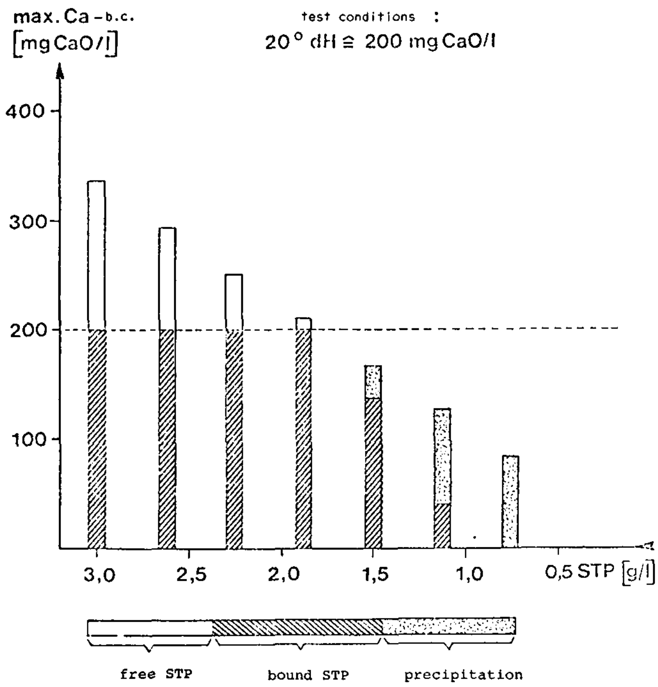

FIG. 1. Phosphate reduction – effects on primary and secondary washing performance.

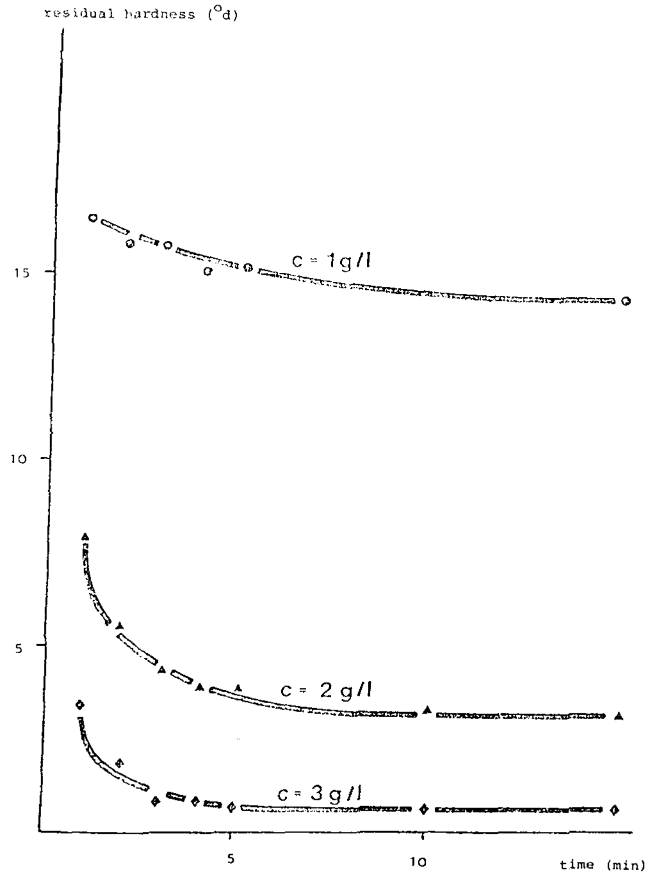

FIG. 2. Kinetics of calcium binding by a sodium aluminum silicate. Initial hardness: 30°d; temperature: 25 C.

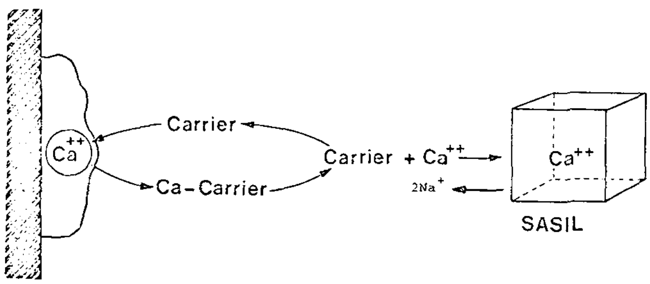

FIG. 3. Carrier mechanism.

sued by the detergent industry. The research data and results on specific sodium aluminum silicates therefore present a totally new alternative in the search for phosphate replacement. In the course of numerous studies we have found that regularly crystallized (cubic) types of sodium aluminum silicates are particularly useful in the washing process, especially certain varieties of zeolite A, which we call SASIL®. Most of the data discussed below have been obtained with zeolite A, which is referred to in particular when we speak of sodium aluminum silicates.

The ion exchange behavior of these sodium aluminum silicates depends on size and hydration of the ions. Not only Ca and Mg ions are exchanged, but also Pb, Cu, Ag, Cd, Zn, and Hg ions. While the elimination of Ca ions, and to a lesser extent of the Mg ions, is of considerable importance for the washing process, the ability to exchange heavy metal ions is to be viewed from an ecological viewpoint, which will be discussed later on.

The ion exchange is not only dependent on ion size, but also on concentration, time, temperature, and pH. Figure 2 shows that the exchange kinetics depend on concentration and time. Ca ions are exchanged in a very short period of time, whereas the exchange of Mg ions takes a little longer. With increasing temperature, however, the rate of exchange increases. This may be explained by the larger hydration shell of the Mg ion, which slows down the exchange at lower temperatures. With increasing temperature, however, the hydration shell becomes smaller.

TABLE II

Property Profiles of Inorganic Builders

A. Water-soluble complexing agents	B. Water-insoluble ion exchangers
Representative example STP	Representative example zeolite A
1. Complexing of multivalent ions	1. Binding capacity for multivalent ions by ion exchange
2. Alkaline reaction	2. Alkaline reaction
3. Specific adsorption to pigments and fibers	3. Adsorption of molecularly dispersed substances
4. Specific electrostatic charges of pigments and fibers	4. Heterocoagulation with pigments
5. Removal of multivalent ions from within the dirt and from fibers	5. Crystallization surface for sparingly soluble compounds
6. Nonspecific electrolyte effects	

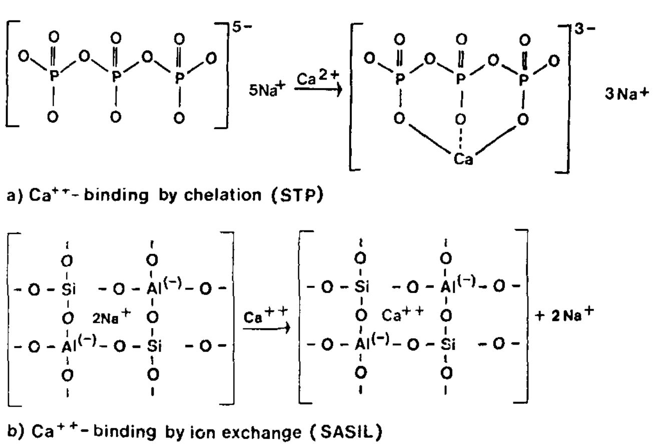

FIG. 4. Ca^{++}-binding by chelation and ion exchange.

According to our present knowledge, the use of sodium aluminum silicates alone, that is to say without further addition of builders, will result in reduced washing performance. Better results are obtained if combinations of sodium aluminum silicate and water-soluble complexing agents are used; these are able to take up multivalent ions – again particularly Ca and Mg ions – from solid surfaces and to pass them on to the ion exchanger sodium aluminum silicate after transport through the aqueous medium. This property can best be explained as a carrier effect with the following stages: (a) sorption of carrier on the interface textile fiber/dirt, (b) complexing of Ca and Mg ions, (c) transport from the solid interface textile fiber/dirt through the wash liquor to the sodium aluminum silicate surface, (d) dissociation of the complex consisting of carrier and Ca and Mg ions, (e) ion exchange of Ca and Mg against Na in the sodium aluminum silicate crystal, (f) sorption of carrier on the interface textile fiber/dirt, (g) complexing of Ca and Mg ions, and so on (Fig. 3).

BINARY BUILDER SYSTEMS

Differences between Water-soluble Complexing Agents and Water-insoluble Ion Exchangers

If we compare the property profiles of water-soluble

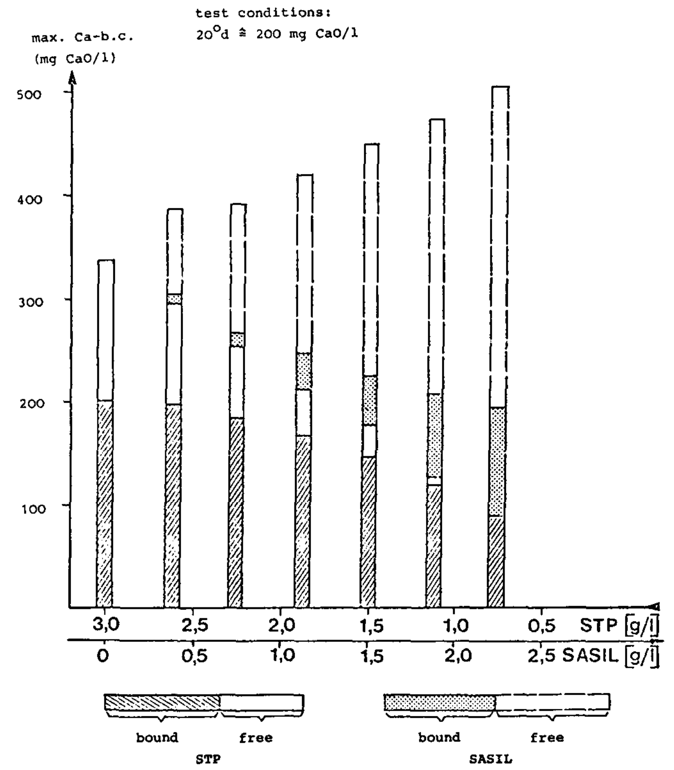

FIG. 5. Interactions in the binary builder system STP/SASIL.

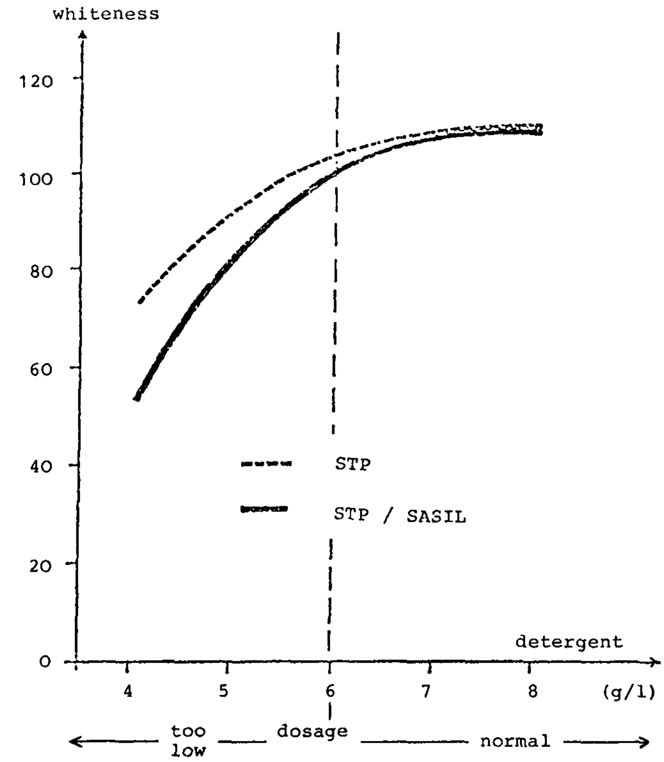

FIG. 6. Washing performance of STP- and STP/SASIL-based heavy duty laundry detergents.

complexing agents and water-insoluble ion exchangers, similarities as well as differences are noticeable (Table II).

The different properties of STP and sodium aluminum silicates can be explained by differences in solubility and in the action mechanism of eliminating the constituents of water hardness. In the case of STP, Ca is bound by chelation, in the case of sodium aluminum silicate, by ion exchange (Fig. 4). Further differences result from the marked adsorption capability of the triphosphate anion.

Interactions between STP and Sodium Aluminum Silicate

In the wash liquor there will be a competitive reaction between the complexing agent STP and the ion exchanger sodium aluminum silicate. In suitable formulations (Fig. 5) the properties of STP and sodium aluminum silicates may complement one another. In the binary builder system both builders contribute to the elimination of Ca and Mg ions. If the phosphate content is reduced, it is important that the STP is not "used up" in complexing of the constituents of water hardness, but that some free STP is available for other processes. The capacity available in the zeolite for the binding of Ca and Mg ions is only partially used. This reserve capacity is important on the one hand, with respect to the "suction effect" concerning Ca and Mg ions, and on the other hand, with respect to the rinsing process, in which further Ca and Mg ions are introduced into the wash liquor with each addition of rinsing water. By the combination of STP and sodium aluminum silicates, the region that is critical with regard to the formation of incrustations with decreasing STP concentrations is significantly lowered. The result is an overall increase of the Ca binding capacity in the binary system of STP/sodium aluminum silicate, which, in turn, has a positive influence on the washing performance.

Surfactant Optimization

The binary builder system STP/SASIL insures excellent *secondary* washing results, that is to say, that incrustations by the precipitation of Ca and Mg phosphate are largely avoided. By a gradual exchange of STP by SASIL in heavy duty laundry detergents, the *primary* washing performance falls off to some extent. However, it is possible not only to compensate for this effect, but even to improve the primary

TABLE III

Toxicological Tests

Objective	Testing method	Result
Toxicity acute	8 days	SASIL is nontoxic – even
subacute	Rat, oral 90 days	at high concentrations
chronic	2 years	from 9/76, to date no effect
Local irritation	Man, mouse, rabbit	No effect slight mechanical irritation, reversible
Inhalation		
Model experiments	Intraperitoneal and intratracheal alveolar macrophages	SASIL is not silicogenic SASIL is an inert dust minimal cytotoxicity
Inhalation experiments	Rat, 90 days	SASIL does not cause histological damage
	Rat, 2 years	from 2/76, to date no effect

TABLE IV

Comparison of Normal Phosphate-based and SASIL-based Laundry Detergents – Toxicological Tests

Objective	Heavy duty laundry detergent	
	With 40% STP	With 20% STP and 20% SASIL
Toxicity rat, oral	$LD_{50} > 5g/kg$	$LD_{50} > 5g/kg$
Dermal irritancy mouse, man patch test	No significant differences following intracutaneous or epicutaneous administration	
Mucous membrane irritancy *rabbit*	*No significant differences*	
Inhalation testing for silicogenic properties	Not tested	After three months: no effect

TABLE V

SASIL – Influence on Biological Sewage Treatment

Objective	Testing method	Result
Aerobic degradation	OECD-screening test compact sewage plant trickling filter	Even at high concentrations no influence on biodegradation
	OECD-confirmatory test	After adaptation of system positive influence
Anaerobic degradation	Laboratory digesters	No influence on the development of digester gas
Nitrification	Confirmatory test in sewage plant	Significantly positive influence of SASIL

TABLE VI

Project: "Environmental Behavior of SASIL" Field Test Stuttgart-Büsnau[a]

Objective	Result	
Composition of sewage	Average concentration of SASIL: 25 mg/l P - load lowered by 55%	
Fate of SASIL	60% Sandtrap and preliminary clarification 34% Biological clarification 6T Effluent	
Influence on sewage treatment efficiency	No influence could be detected, results:	
	Decrease MBAS	94%
	Decrease BiAS	91%
	COD-decrease	81%
	BOD-decrease	96%
	Retention P	17%
	Retention N	33%
	Nitrification and sludge treatment	Unchanged

[a]Duration of test: March 1976-March 1977.

washing performance by suitably optimizing the formulation with regard to the surfactants (Fig. 6).

Types and amounts of surface-active agents are important factors. Combinations of anionic with nonionic surfactants as well as special combinations solely based on lower and higher ethoxylated fatty alcohols have been shown to be particularly suitable.

Field Tests

Heavy duty laundry detergents, based on the binary builder system STP/SASIL with optimized formulations were studied in model experiments, and subsequently tested in panel tests and on test markets. The complete removal of the new water-insoluble ingredients was given special attention. As it turned out, no deposits of SASIL could be observed in washing machines or on textiles. Systematic analyses have shown a good consumer acceptance of the new laundry detergent.

MANUFACTURE AND PROCESSING OF SODIUM ALUMINUM SILICATES

Technical Manufacture

There are two possibilities for the large-scale production of sodium aluminum silicates:

1. reaction of sodium silicate with sodium aluminate in an aqueous alkaline solution

$$\underset{\text{sodium silicate}}{Na_2SiO_3 \cdot xH_2O} + \underset{\text{sodium aluminate}}{NaAlO_2 \cdot xH_2O} \xrightarrow{NaOH} \cdot \xrightarrow{xH_2O}$$

$$Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O$$

SASIL (empiric formula)

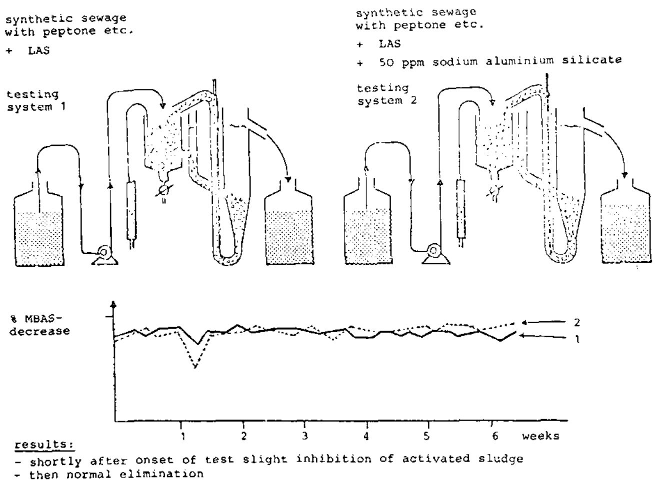

FIG. 7. Effect of sodium aluminum silicates on biological treatment (experimental model using modified OECD-confirmatory test.) Results: (a) Shortly after onset of test slight inhibition of activated sludge, then normal elimination.

2. hydrothermal conversion of kaolin in concentrated sodium hydroxide

$$\underset{\text{kaolin}}{Al_2O_3 \cdot 2SiO_2} \xrightarrow{NaOH} \cdot \xrightarrow{xH_2O} \underset{\text{SASIL (empiric formula)}}{Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot xH_2O}$$

Both processes are technically feasible but further discussion is not possible in the time allowed here.

In the manufacture of SASIL-based detergents, the new raw material may be introduced via the slurry in the usual spray drying process. There is no need for technological changes.

ENVIRONMENTAL BEHAVIOR

The large-scale use of sodium aluminum silicates in laundry detergents is dependent on the proof of toxicological and ecological safety. Our testing programs were designed to meet international requirements for the clearance of new chemicals.

Studies to Establish Toxicological Safety

The studies ranged from the determination of acute, subacute, and chronic toxicity to inhalation studies (Table III). With reservation as to the outcome of the long term toxicity results, it may be said that nothing has been found that might deter the use of SASIL in detergents. Results of the 2-year feeding study and the 2-year inhalation studies are expected by the end of 1978.

The studies included not only the compilation of the toxicological data of SASIL, but also of SASIL-based detergents. Comparative testing of normal phosphate-based and low-phosphate/SASIL-based detergents revealed no toxicological differences, which means that there should be no health hazard for the consumer of SASIL-based laundry detergents (Table IV).

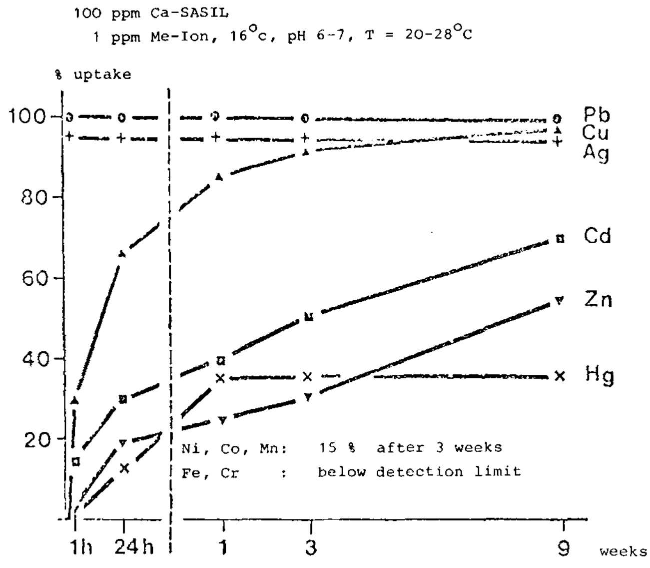

FIG. 8. Ion-exchange behavior of SASIL.

Studies to Establish Ecological Safety

Ecological studies ranged from model experiments to extensive field tests. Here, the crucial questions concerned the possibility of sedimentation of SASIL in household or communal sewerage systems, or a possible impact of SASIL on aquatic systems or the operation of sewage treatment plants. Another crucial point was the question of heavy metals being remobilized from lake and river sediments.

TABLE VII

SASIL – Chronic Toxicity to Water Organisms

Organism	Testing method	Result
Algae	AAP-test in shaking flask and field tests	Not toxic; no stimulation of algal growth
Water-fleas	Slowly rotating flask	No effect, normal life cycles
Mussels and tubifex	Laboratory river model	No effect, no accumulation
Fish	Aquarium, arena basin, artificial lake	Not toxic

TABLE VIII

SASIL – Uptake and Release of Heavy Metals (Me)

Medium	Testing method	Result
Normal (mineral) water – synthetic tap water, 16°d	Stirring of SASIL and Me in closed system	Me/SASIL – binding; no complete desorption or remobilization
Municipal sewage – pretreated	Flow system pressure filter	Significant uptake of added Me, minimal remobilization
River water – Rhine	Shaking in closed system exclusion of oxygen	No remobilization of sediment-bound Me by SASIL

Luckily, the ecological studies showed nothing that might prevent the use of SASIL in detergents. No evidence of sedimentation of SASIL was found in either the product tests or the large-scale field test of 1-year duration in Stuttgart-Büsnau. The 960 households connected to the municipal sewage treatment plant, which serves research and teaching purposes, were provided exclusively with a SASIL-based detergent. No negative influence of SASIL on biological wastewater treatment could be found; on the contrary, significantly positive effects were encountered in the biodegradation of surfactants in the OECD confirmatory test and in the nitrification process (Tables V and VI and Fig. 7).

During the 1-year large-scale test in Stuttgart-Büsnau no influence of SASIL on the operation of the sewage treatment plant could be found. SASIL was almost quantitatively eliminated in the process of wastewater treatment. SASIL is nontoxic to water organisms (Table VII).

As mentioned above, ion exchange by SASIL is not limited to Ca and Mg ions; heavy metals are also exchanged. This effect contributes considerably to the detoxification of wastewater. However, the question of recycling heavy metal/SASIL containing sewage sludges for agricultural use remains to be clarified. A final answer to this question can only be given after several agricultural cycles (Table VIII and Fig. 8).

MACRO-ECONOMICAL CONSIDERATIONS

STP is an ideal builder in laundry detergents, which significantly contributes to meet the requirements of hygiene and cleanliness. Because of the contribution of phosphates to the eutrophication of surface waters, detergent phosphate limitations and bans are to be expected in Europe and in the U.S., regardless of the fact that chemical precipitation of phosphates in sewage treatment plants is the more effective approach to solve the problem. The addition of tertiary treatment to existing sewage treatment plants will cause additional expenses in the order of 10% of the cost of mechanical and biological sewage treatment.

The partial replacement of STP by sodium aluminum silicates will not solve the eutrophication problem. What will be achieved, however, is a decrease in the total amount of phosphates entering the surface waters. Also, SASIL is fairly easily accessible today. Manufacturing costs of STP and sodium aluminum silicates may be in the same order of magnitude. Thus, the costs of low-phosphate SASIL-based laundry detergents may be influenced by the location of the production facilities and surfactant optimization (amount and nature of the surfactants used). In spite of the very considerable expenses incurred both in research and development and in the investigation of the environmental behavior, the use of sodium aluminum silicates in laundry detergents will not have any negative macro-economical consequences.

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