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CEMENT-POLYMER MATERIALS FOR WELL CASTING

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The efficiency of using the SCADC reagent as an additive in the cement-polymer mixtures has been shown. The physical and mechanical properties of the cement slurry and the stone, formed on their basis at the temperatures of 22°C and 80°C have been presented. The main regularities of the formation of the structures of various levels in the cement-polymer mortars have been revealed, depending on the degree of filling and the type of the introduced modifications of the SCADC reagent. It has been found that an entangled fibrous structure is formed between the hydrated cement minerals and the complex additive SCADC. At a concentration of 0.2%, it provides a "self-healing effect" for a damaged cement stone, and also improves the properties of the cement-polymer grouting mixtures, contributing to a decrease in the filtration rate of the mortar down to 30%, an increase by 25-27% in the bending strength and by 36-42% in the ultimate compression strength.

Keywords: cement-polymer material, cement slurry, cement, cement additive.

Introduction

Despite the many years' history of the oil and gas industry, practically the only widely used grouting material is Portland cement, which is a mixture of minerals obtained by baking a rationally selected mixture of limestone, clay, and corrective additives [1–4]. Its main advantages over the other backfill materials are its well-controlled slump time followed by hardening and stone formation. Unfortunately, the stone obtained from Portland cement has many significant drawbacks, which necessitate the search for more promising materials. Most often, the researchers look to polymeric materials, which are often used in amounts up to 0.5–1.0% to control the individual technological properties of the resulting mortars and stone [5–8]. The mechanism of action of many polymers in cement slurries is associated with the binding of an excess amount of water, plasticizing, or hardening effects due to the formation of their discrete phases, homogeneously mixed with cement gel [9].

At the same time, there are practically no studies, which consider the intermolecular interaction of the cement hydration products and polymer, and the formation of complex structures, which have advantages over both the cement hydration products and polymerization products.

Theoretical aspects

In general, cement-polymer and polymer-cement materials are mixtures of cement and polymer with or without fillers in various proportions, hardened in the presence of water. Depending on the required properties, stabilizers, plasticizers, catalysts, hardening accelerators, and other auxiliary additives are added into the polymer cement composition.

A generally accepted indicator of the quality of the types of polymer cement is the polymer cement ratio (P/C), equal to the ratio of polymer and cement (inorganic binder). It is noted in [10] that the binder in the formed stone is the matrix phase, which contains cement gel and a polymer film.

Thermoplastic polymers (polyvinyl acetate, acrylic polymers) and rubbers are used as polymer components in polymer cement materials, as well as oligomeric thermosetting resins (epoxy, carbamide) and monomeric products, which, under the influence of hardeners or other hardening initiators (temperature, pH, etc.) are converted into polymeric products [11].

When choosing polymers, we took into account the following requirements:

- water solubility and permeability at temperatures up to 90°C;

- stability upon the contact with chemically active substances contained in the formation waters;
- preservation of the physical and mechanical properties of cement mortar and stone.

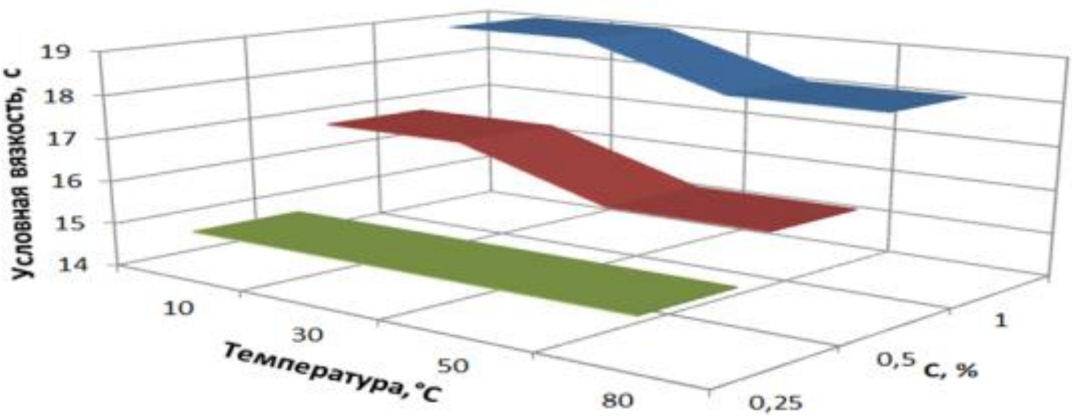
The above requirements are most fully met by a complex reagent - a copolymer of acrylamide and diallyldimethylammonium chloride (hereinafter referred to as the SCADC), which makes it possible to obtain suspensions on its basis with a wide range of ratios of the liquid and solid phases, each of which can participate in the process of formation of the structure of the final product [12, 13]. Moreover, various modifications of the complex reagent can be obtained, depending on the synthesis characteristics.

The resulting reagent may be granules, a fine powder, or an aqueous dispersion mortar. The linear structure of the molecules stipulates an ability of the reagent not only to swell but also to dissolve in the appropriate solvents.

The hydrophobic reagent SCADC is a partially cross-linked copolymer, containing macromolecules with the sizes of 0.15–0.42 μm (15%) and 0.028 μm (85%). It can absorb water in an amount, exceeding its own from 100 to 1000 times, and retain it in its structure.

The hydrophilic reagent SCADC is highly soluble in cold water and the reservoir water, forming a jelly-like aqueous mortar, which is resistant to salts of polyvalent metals, to mineralized waters, and elevated temperatures (up to 250°C). The low viscosity of the mortar, corresponding to the water viscosity, allows it to penetrate well into cracks and fill them. The reagent is compatible with both aqueous and non-aqueous mortars such as diesel and petroleum. It does not require retarders or activators. Its thermal stability exceeds 230°C. An important factor in polymerization is the pH value of the reaction medium. Thus, to obtain water-insoluble cross-linked polymers by forming amide bridges –CO–NH–CO– between the AA macromolecules, an acidic medium, and high temperatures are required, and to obtain partially hydrolyzed PAA, the presence of an alkaline medium is required, in which the hydrolysis of amide groups occurs [13].

The low concentration of 0.1–0.3% of the water-based SCADC mortars are Newtonian liquids. An increase in the concentration up to 0.5–1.0% significantly increases the viscosity of the mortars, and the nature of their flow becomes close to the non-Newtonian one (Fig. 1).



- *Hydrophobic polymer*
- *Complex polymer addition*
- *Hydrophilic polymer*

Figure 1. The effect of the SCADC reagent on the relative viscosity of the mortars

As for the interaction of the cement hydration products and the polymer reagent, the following can be noted: as cement stone hydrates, crystalline hydrates (hydration products) grow on the surface of the polymer grains, which increases the polymer material strength. It has been shown in the paper [11] that as free water in suspension decreases, the polymer forms a thin film on the surface of pores, capillaries, grains of cement, and filler, which is characterized by high adhesion and initiates an increase in the adhesion of fillers (inert additives) and a cement stone, which improves by order the solidity of the resulting stone and the state of its mineral skeleton. In this case, the strength of the crystallization structure is determined, on the one hand, by the intergrowth of the crystals of new growths of calcium hydro silicates of different basicity, drawing together, and, on the other hand, by the formation of polymeric dendrite-like growths and filamentary anisometric crystals. The mutual intergrowth of these structures, their interlacing provides a synergistic effect, as a result of which the cement-polymer stone acquires an increased compressive strength, and especially in bending and compression, high adhesive characteristics, impermeability, etc., in comparison with the conventional stone.

The authors of the paper [9] have emphasized that the mineral and high-polymer binders enter into chemical reactions with each other. The results of thermographic studies have allowed them to conclude that the organic polymer has been strengthened by hydrate new growths. Due to the high adhesive and cohesive qualities, the polymer can combine mineral fractions and cement new growths into a single conglomerate, and cement, which has a significant proportion in the mixture, plays the role of a micro filler.

Experimental studies

Portland cement has been used in the studies as a binder, which meets the requirements of GOST 1581-96 [14]. Portland cement of the type PCT-1-50 and PCT-1G-SS-1 has been used in this work.

It is expedient to use the SCADC additive in the composition of the backfill material, assuming a possibility of the formation of the additional polymer bonds with the products of hydration and hardening of cement, represented by calcium hydro silicates, calcium hydro aluminates, and other crystalline hydrates [3, 4].

The dynamics of changes in the particle size of the SCADC reagent in the neutral medium (pH = 7) are shown in Fig. 2.

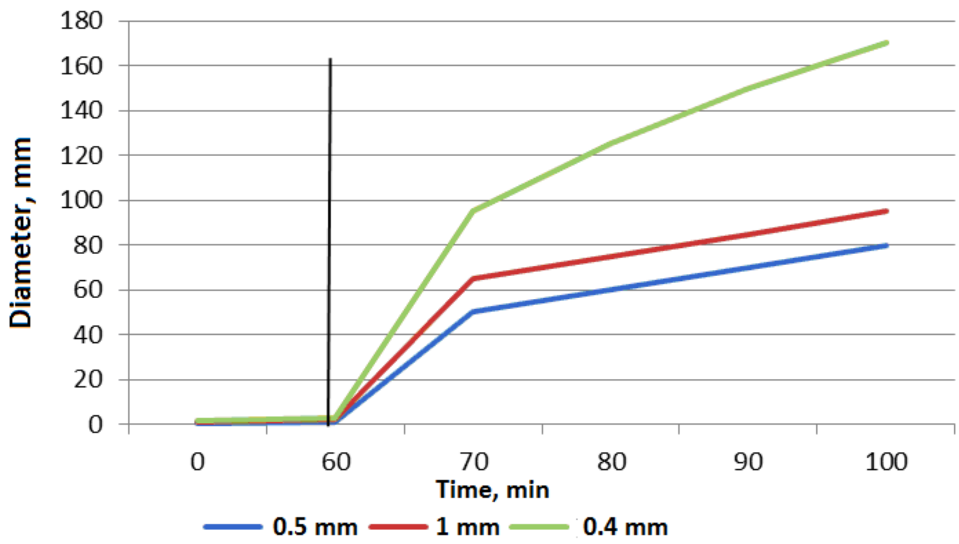


Figure 2. The effect of the particle size of the SCADC reagent on the kinetics of their swelling

It is seen from Fig. 2 that the particles of the SCADC reagent significantly increase in size after 60 min of exposure to water. Changing the pH of the medium above or below 7 reduces the degree of swelling of the SCADC reagent.

The effect of the particle size of the SCADC reagent on the strength of the cement-polymer stone (Fig. 3) has shown a decrease in its strength with an increase in the particle size of the SCADC reagent. The highest strength of the stone, obtained with the diameter of d_o = 0.5 mm, allows us to recommend it as the most optimal in terms of the strength-water absorption ratio and sufficient for the “self-healing effect” [15, 16].

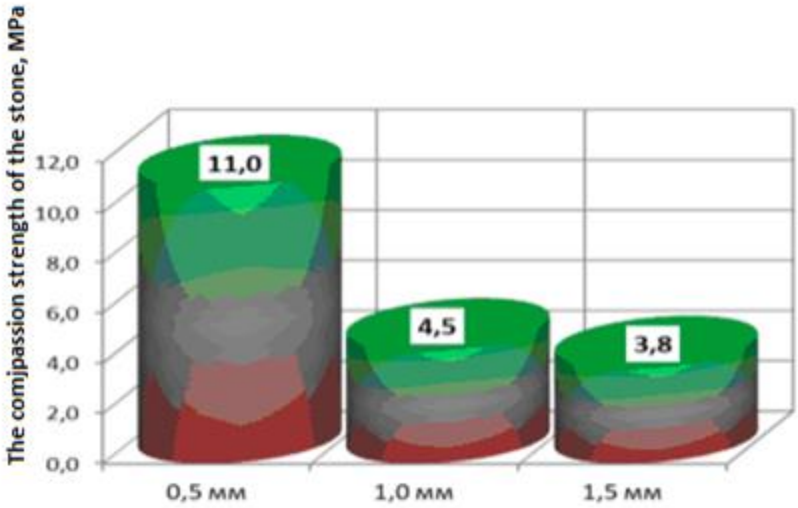


Figure 3. The effect of the particle size of the SCADC reagent on the strength of the cement-polymer stone

An analysis of the structure of the cement stone has revealed significant differences in the SCADC reagent inside the stone at various concentrations. At the concentration of the SCADC reagent of 0.1–0.3% of the binder mass, one can observe a reduction in the size of the cross-section of crystals of both primary and secondary generations in the photographs taken with an electron microscope. In the main volume of the sample, the proportion of the acicular products increases (Fig. 4), and the structure of the plugging stone acquires a tangled-fibrous appearance (Fig. 5), which is extremely rare in cement stone without this reagent. The maximum content of the acicular crystals is marked at the concentration of the SCADC reagent of 0.1–1.0% of the binder, and it is this cement composition that is characterized by the maximum bending strength.

The hydrophilic form of the SCADC reagent has a high solubility in water, where its molecules form the additional centers of crystallization of filamentary new growths. This feature of the SCADC reagent has a positive effect on the strength of the cement stone, as well as on its adhesive characteristics. According to the results of G.V. Berezhkova [17], whiskers are characterized by increased elasticity and strength as compared to microcrystals. This explains the role of the SCADC reagent in the process of the formation of fine varieties of hydrosulfate aluminates and the increase in the strength of the cement stone when the content of the SCADC reagent is 0.1–1.0%.

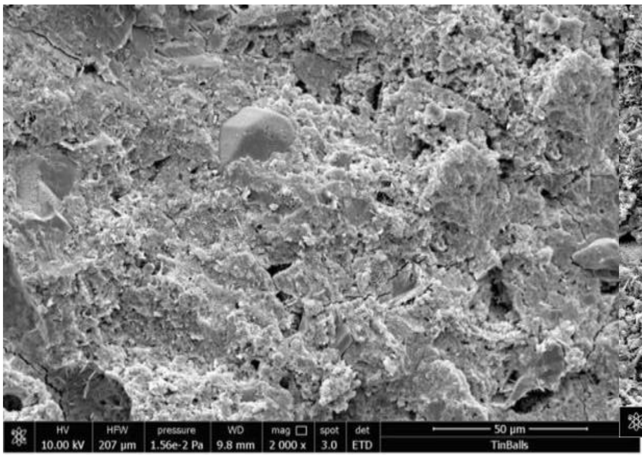


Figure 4. Acicular products in the cement-polymer stone

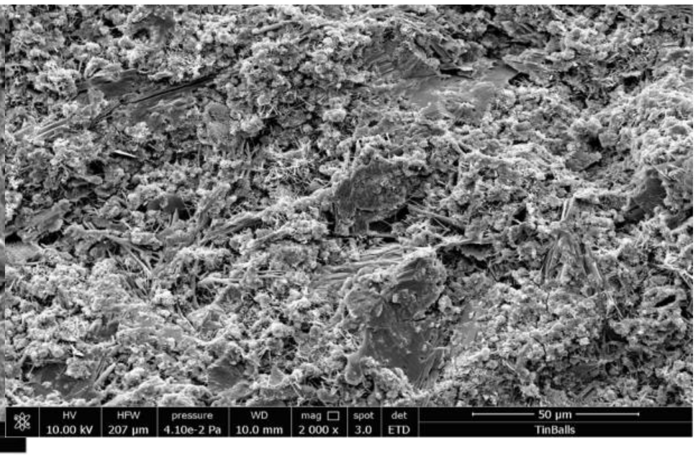


Figure 5. The structure of the cement-polymer stone

With an increase in the content of the SCADC reagent by more than 1%, a deterioration in the strength properties of the cement stone is observed. Finely dispersed deformed-stressed hydro silicate structures (minerals) of various structures are formed in the samples. These minerals lead to the appearance of additional internal stresses leading to the destruction of the crystalline framework. Similar crystals have been observed in all samples without exception, containing SCADC reagent at a concentration of more than 1%.

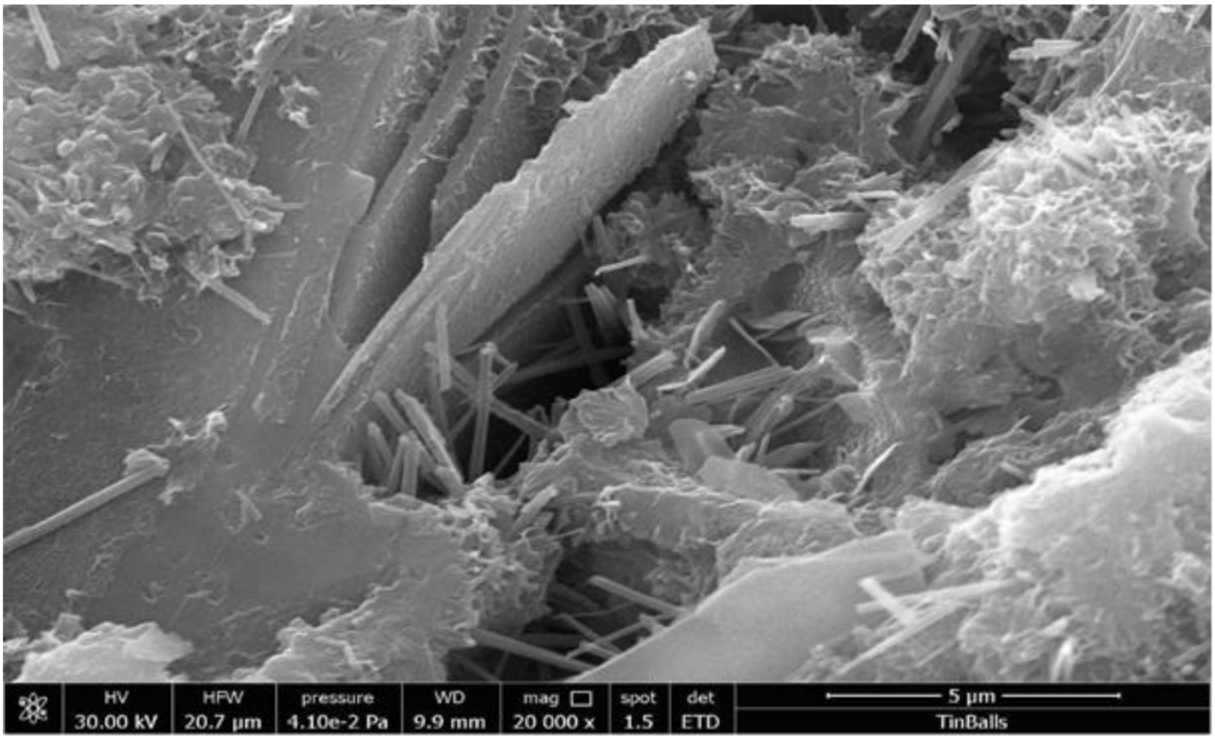


Figure 6. Large mineral crystals formed as a result of adhesion of the polymerization products

It is seen in Fig. 6 that the large crystals of the mineral are formed due to the consolidation of the small ones. At the same time, it should be noted that such a mechanism of their growth is fixed both in the samples of cement stone and without the addition of the SCADC reagent, but it does not have a mass character and does not significantly affect the change in the stone strength.

Designs of the cement-polymer systems

At the first stage of the study, the concentration of the SCADC reagent has been optimized. The temperature, concentration of the SCADC reagent, and duration of the studies have been taken to be the main parameters for the hardening of the cement-polymer mixture. The temperature of the process has varied from 22°C to 80°C, the duration has made up from 1 to 28 days, the concentration of the SCADC reagent has varied from 0.1% to 1.0%. The compressive strength of the cement stone has been taken as an optimization criterion.

The following symbols have been introduced: CHS - Portland cement (hereinafter - PC) with the addition of the SCADC reagent in a hydrophobic state (water-swellable); CHL - PC with the addition of the SCADC reagent in the hydrophilic (liquid) state; CMH - PC with the addition of the SCADC reagent in a complex form (water-swellable and liquid state).

The research results are presented in Tables1 and 2.

Table 1. Properties of the Portland cement mortar and stone with the addition of 0.2% of the SCADC reagent in the complex form (T = 22°C)

Characteristic	W/C*			
	0.5	**0.6**	**0.8**	**1.0**
Mortar density, kg/m³	1850	1700	1600	1500
Spreadability, mm	250	250	250	250
Hardening time, min	240–250	300–310	330–360	400–450
Ultimate strength after 2days, MPa				
– upon bending	6.9	5.3	4.2	3.6
– upon compression	23	22.2	13.2	11.2

**W/C – water/cement*

It is seen from Table 1 that the spreadability of the cement slurry practically does not change when 0.2% of the SCADC reagent in a complex form is introduced therein.

The results of the study of the filtration properties of the cement-polymer mixtures at the temperature of 22°C are presented in Table 2, and an estimate of the hardening rate is presented in Table 3.

An analysis of the sedimentation features in the inclined-directed, low-angle, and horizontal wells (Table 2) has shown that at the concentration of 0.2% of the SCADC reagent in various modifications, there is no water separation in the cement slurry, and the filtrate recovery does not exceed 70 cm^{3}for 30 minutes.

At the same time, the grouting slurry with various types of grouting cement and the addition of the SCADC reagent at the concentration of 0.2% meets the requirements of the customers in terms of setting time.

The parameters of the cement-polymer slurry obtained during the tests at the temperature of 80°C are summarized in Tables 4–6.

Table 2. The effect of the SCADC reagent on the filtration properties of the cement slurries

Type of the binder	Conditional water loss, cm^3/30min	Water separation at the cylinder inclination angle of 45°, ml
PCT-1-50	440	14,0
CHS	60	0
CHL	50	0
CMH	43	0

PCT-1G-CC-1	644	5.0
CHS	70	0
CHL	50	0
CMH	50	0

Note: density of the PCT-1-50 mortar and binders based thereon is 1850 kg/m^3, density of the PCT-1G-SS-1 mortar and binders based thereon is 1900 kg/m^3

Table 3. Setting times for the cement-polymer mixtures

Composition	W/C	Setting times at 22°C, h-min,	
		start	end
PCT-1-50	0.50	4-30	7-00
PCT-1-50+$CaCl_2$–2%	0.50	2-40	4-00
PCT-1-50+0.2% MH	0.50	4-30	7-30
PCT-1G-CC-1	0.44	5-20	7-50
PCT-1G-CC-1+0,2% MH	0.44	6-00	8-40

Conclusion

It is theoretically substantiated and experimentally confirmed that the cement-polymer materials with the addition of acrylamide and diallyldimethylammonium chloride copolymer (the SCADC reagent) at the concentration of 0.2% to the cement slurry can be effectively used to improve the quality of casing of various wells.

The cement slurries obtained from the cement-polymer mixtures from the well cement of the PCT-1G-CC-1 type and the SCADC reagent make it possible to increase the strength of the resulting stone, its adhesion to the casing column, and also significantly reduce the filtration of the mixing fluid into the reservoirs.

The technology for preparing and pumping the proposed mortar does not differ from the technology, used when working with the cement mortars, i.e. the standard machinery and equipment are used. No special equipment is required to perform work in the well. The quantity and characteristics of the mortar depend on the work conditions and are selected in the laboratory tests.

Table 4. Parameters of the cement-polymer cement slurry based on PCT-1G-CC-1 at the temperature of 80°C

No	Additives, %	Spreadability, mm	Density, kg/m^3	PV, cPs	BPS, Pa	Setting time, h-min	
						start	end
1	–	>250	1900	20	5	1-50	2-20
2	0.2 HphobC	250	1900	20	5	2-00	4-40
3	0.2 HphilC	250	1900	20	5	2-30	5-20
4	0.2 WL	250	1900	20	5	2-30	5-20

Symbols:
HphobC – hydrophobic condition;
HphilC– hydrophilic condition;
WL – water-swellable and liquid condition

Table 5. The effect of the SCADC additive on the permeability of the cement-polymer cement slurry based on PCT-1G-CC-1 at the temperature of 80°C

No	Additives, %	Density	Thickening, h-min		
		kg/m³	30vs	50vs	70vs
1	**–**	**1900**	**1-30**	**not measured**	**not measured**
2	0.2 HphobC	1900	2-00	3-10	4-30
3	0.2 HphilC	1900	2-30	2-50	5-10
4	0.2 WL	1900	2-15	2-25	5-00

Table 6. Properties of the cement-polymer stone based on PCT-1G-CC-1 at the temperature of 80°C

No	Additives, %	Mortar density, kg/m³	Tensile strength, MPa after						Adhesion to metal, MPa after		
			1day		2day		24days		1day	2days	24days
			under bending	under compression	under bending	under compression	under bending	under compression			
1	–	1900	3.3	11.0	3.5	14.9	4.5	20.0	4.1	4.4	4.9
2	0.2 HphobC	1900	4.6	15.2	6.1	16.9	7.6	42.5	4.5	5.1	6.0
3	0.2 HphilC	1900	5.1	16.1	6.9	18.1	8.1	44.1	5.1	5.5	6.7
4	0.2 WL	1900	5.3	16.2	7.2	18.1	8.3	44.2	5.5	5.6	7.0

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