MODEL EXPERIMENTAL DE RECICLARE A UNUI DEŞEU DIN INDUSTRIA HÂRTIEI CA MATERIE PRIMĂ SECUNDARĂ ÎN BETON

AN EXPERIMENTAL MODEL OF WASTE RECYCLING FROM PAPER INDUSTRY AS SECONDARY RAW MATERIAL IN CONCRETE

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This paper reports on the results of a research about utilization of inorganic sludge (IS) produced by paper industry as cement and fine sand substitute secondary raw material in concrete. The inorganic sludge IS valorization as cement partial substitute into concrete has been supported by experimental data concerning the pozzolanic potential evaluated by Al and Si content of IS waste compounds solubility into leachant of pH=12 and by the compressive strengths time evolution. The concrete samples with the addition of inorganic sludge from paper industry have been characterized by overtime variation of the following characteristics: water absorption, dimensional changes, compressive and flexural strengths. There have also been determined leaching properties by monolithic leaching test. The evolution of the physical and mechanical characteristics suggest the inorganic sludge can be used as a substitute for fine sand in concrete in an amount up 50%, and / or substitution of up to 20% cement. The heavy metal leaching properties measured by the concrete monolithic samples leaching test with the highest content of IS, showed a heavy metal Pb, Cr and Cu release trend diminishing during time, after a logarithmic plot.

Articolul conţine date experimentale referitoare la utilizarea nămolului anorganic din industria hârtiei (IS) ca materie primă secundară, de substituţie a cimentului şi a nisipului fin în beton. Valorificarea nămolului anorganic, IS, în beton, ca substituient parţial al cimentului a fost susţinută de potenţialul puzzolanic evaluat experimental prin metoda solubilizării aluminosilicaţilor din nămol la pH=12 şi prin evoluţia rezistenţei la compresiune. Betoanele cu adaos de nămol anorganic din industria hârtiei au fost caracterizate prin evoluţia în timp a caracteristicilor următoare: absorbţia de apă, variaţia dimensională, rezistenţele mecanice şi proprietăţile de mediu (prin test de lixiviere pe probe monolitice). Evoluţia caracteristicilor fizico-mecanice sugerează că nămolul anorganic poate fi utilizat în beton ca substituient al nisipului fin în proporţie de până 50% şi /sau ca substituient al cimentului până la maximum 20 %. Proprietăţile de mediu evaluate prin testul de lixiviere pe probe monolit, din betonul cu cel mai mare conţinut de IS, au indicat că metalele grele Pb, Cr şi Cu prezintă o tendinţă de diminuare a solubilizării în timp, după o curbă logaritmică.

Keywords: *Inorganic sludge from paper industry, pozzolana, concrete, leaching, mechanical properties*

1. Introduction

The valorization of the industrial waste by the Romanian local construction industry has become a national priority, as a viable alternative of the disposal and to protect primary resources. But, according to the CP 305/2011 [1] construction products must satisfy specified basic requirements (BR). To comply with BR3, on hygiene, health and environment, the construction products must be applied, as engineering works, so as to not harm health, safety of workers or occupants and the environment.

European pulp and paper industry produce yearly eleven millions tones of waste, of which 70% from the production of deinked recycled paper [2].
Paper sludge generated by the paper industry is composed of organic fibers, inorganic sludge and coating materials (kaolinite, limestone, talc). The inorganic sludge (IS) is usually disposed in landfills or open dumps.

The cement matrix may be compatible with the inorganic wastes resulted from the pulp and paper industry. These wastes, granular or powder can be used as fine aggregate, filler (replacement of fine sand) and/or partial or total substitutes of the cement, according to the application type in constructions.

The addition of 5-15% of paper sludge in the case of brick production improves both the final product and the process [2].

The recycling was directed towards geotechnical and foundations works as roads infrastructure, filling the underground cavities (mines, abandoned tunnels) and those at the surface of the exhausted quarries or in conservation [3, 4].

The use of industrial inorganic waste as concrete addition must be correlated with ecological and technical properties. Also, it is known that waste addition can negatively influences the concrete physical-mechanical

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properties and durability [5-8].

The industrial inorganic waste recycling implies activities based on a laborious research programme, on long term, which examines two main groups of properties such as:

- The environmental properties, which predict and establish the contaminants release into underground and surface water.
- The engineering properties required by the technical and technological parameters of the application field – concrete works, geotechnical, road infrastructure, as according to standard regulations.

The valorization of the paper and pulp industry inorganic sludge as addition in concrete may be considered an interesting area of the industrial waste management.

The focus of this work is to evaluate the use of the IS waste from pulp and paper industry as addition in cement composites as pastes (grouts) and concrete type. So, the treated inorganic sludge by drying and sieving was utilized as partial substitute of the cement and/or of the fine sand of concrete mixes. The concrete with IS addition engineering performances and leaching properties referring to the release of substances that are hazardous to health and environment controls the ability to be used as construction product, according to Construction Products Directive [9]. This research can be considered an attempt to evaluate both the IS contaminants immobilize by concrete cement matrix and recovered IS waste use as alternative material of partially substitute of the cement and/or fine sand in concrete.

2. Experimental part

2.1. Materials

The inorganic sludge (IS) waste content was 64% solid and 36% water. The chemical composition of the dried IS waste was of 96.8% inorganic compounds, 3.8% organic compounds and 3.2% insoluble in HCl (as according to supplier technical report). The IS was processed in order to be used as secondary raw materials for cement based composites. It was dried, sieved and separated on grain size particle grades. The IS waste of 0-1mm particle size was used as fine natural sand substitute and the <1mm particle size IS was used as substitute of fine sand and as pozzolana powder too.

The pastes and concretes with IS waste were carried out with Portland cement type CEM II/A-S 42.5R according to [10].

The river aggregates particle size distribution, 0-4mm sand and 4-8mm gravel, were used according to [11].

A superplasicizer, high range water reducing (HRWR) admixture based on modified polyethercarboxilate was used to prepare the concrete mixes.

The pozzolanic index was calculated with formula (1):

2.2. Methods

The IS waste was investigated by thermal analysis technique. The TGA (*Shimadzu DTG-TA-50H*) was used in order to study the composition of waste. Samples were ground into a fine powder and then 40–50 mg was loaded into an alumina crucible for analysis. The furnace temperature was programmed to rise from ambient to 1000°C at a heating rate of 10°C/min.

The leaching properties of IS waste were tested by a modified dynamic extraction leaching test at own IS waste pH and at pH=12 of the leachant. The liquid to solid (L/S) ratio had values of 10, 30 and 100. The dried sample of IS waste material of 16 g (<1 mm particle size) was immersed into the leachant (demineralized water), for testing contaminant release at own pH of the IS waste, and into NaOH 0.1 N solution with pH=12. The suspension was shacked for 24 hours. The NaOH 0.1 N leachant was used to simulate the situation of the high basic pH of 12-12.5 of concrete matrix pore aqueous solution. This leaching procedure, based on high basic pH leachant, can be relevant in some applications e.g. the cement-based construction products with alternative materials [12, 13].

The monolithic leaching test (MLT) was used to testing the leaching behavior of the IS waste addition concrete according to [14, 15]. The 28 days - hardened concrete samples cubes of 100 mm edge were immersed in demineralised water. The leaching test parameters were: 20°C ± 5°C temperature - the V/A (volume/area) ratio 8 ml/cm^2 and the test total duration of 64 days. The eluate fraction was recovered after the filtration on membrane filter of 0.45 µm. A part of the eluate was used to measuring pH and electrical conductivity and other eluate part was used to analyze concentration of the chemical species by inductively coupled plasma spectrometer or mass spectrometry.

The MLT leach obtained data were used to describe IS waste addition cementitious matrix concrete ability to immobilize contaminants on long term and to characterize the mass transfer mechanism at the interface solid/watery environment.

Pozzolanic characteristics of the IS waste were evaluated by different methods, such as pozzolanic activity index method, by the Al and Si of IS waste compounds solubility into leachant of pH=12 and by measurement of the compressive strengths time evolution of the hardened pastes with IS addition as sand substitute compared to the reference, free of IS.

The pozzolanic activity index was tested according to [16]. The mortar samples (at least three samples per mix) are cured 24 hours in moist environment, 4 days in water at 20°C, 46 hours in water at 50°C, 2 hours in water at 20°C. After that the samples were tested to compressive strength.

$$I = \frac{f_{c1}}{f_{c2}} \times 100 \qquad (1)$$

Where: f_{c1} is the compressive strength of mortar samples with 75% cement and 25% IS addition;

f_{c2} - the compressive strength of reference cement mortar samples.

Also, IS waste was compared with a glass powder, which is a veritable pozzolana due to the reactive silica, in vitreous state. In this way, there were carried out three mixes with 25% cement and 75% different powders as following: of fine sand (A2N), of glass powder with <0.2 mm particle size (A2E) and with IS waste powder (A2). These pastes were molded into 2 cm edge cubes, (12 samples of each mix) and cured in water at room temperature. The 180 days-compressive strength of mixes was the criterion to estimate IS waste pozzolanic potential, comparatively with those of glass powder.

On the other hand, the pozzolanic potential of IS waste was tested for Si and Al solubility in demineralized water at own pH and into basic leachant (NaOH 0.1 N).

The physical and mechanical properties of the concretes – the water absorption, the dimensional changes and the compressive and flexural strengths were tested.

The water absorption by immersion was tested as according to [17]. The test specimens were kept submerged at 20 ± 5°C until testing time when it was measured the weight of samples (Ms). The specimens are dried at 105±5°C until constant mass was achieved (M_{wd}). Water absorption by immersion measured was calculated by means of:

$$WA = \frac{M_s - M_{wd}}{M_{wd}} \cdot 100 \qquad (2)$$

The compressive strength of the hardened concrete was determined at different ages on 100 mm edge cubes. These cubes were removed from the moulds after 1 day and were cured in water at 20±5°C before testing [18]. At the given ages, three specimens per mix were subjected to compressive strength testing, using WPM 30T/F and WPM 300KN machines. The strength results were presented as the average of the three specimens.

The flexural strength was determined by testing the 100x100x550 mm prisms cured in the same conditions as samples of compressive strength test according to [19].

The dimensional changes as concrete shrinkage or expansion during time, were measured on 40x40x160 mm prisms (three samples for each concrete mix) using a microcomparator device.

The mix design of concrete

It was prepared three mix of concretes with IS waste addition and a reference concrete mix free of waste.

In Table 1 are presented the concrete mixes as following: A22 with IS waste as substitute for 20% of cement and for 20% of fine sand; A25 with IS waste as substitute for 20% cement and for 50% of fine sand and A05 with IS as substitute for 50% of fine sand.

3. Results and discussion

3.1. Inorganic sludge characterization

The thermal analysis DTG curve main peak showed an endothermic effect from 670°C to 900°C, with a maximum at 881°C, according to the decomposition of the calcium carbonate, and a mass loss of 38.28%. Up to 670°C the mass loss was small, 3.32%, without any endothermic effect.

The IS physical characteristics, particle size dimension and, density were determined. The results are showed in Table 2.

The chemical composition of inorganic sludge as resulted in the causticising process and disposed to landfill, according to data from CEPROHART, is shown in Table 3.

The pozzolanic potential of IS waste was tested by various methods.

The obtained pozzolanic activity index has an acceptable value of 78.8% as pozzolanic material (a regular pozzolana activity index value is at least 85%, according to [16]).

Table 1

The concrete mixes and fresh concrete properties/*Compoziții ale betoanelor studiate şi proprietățile acestora în stare proaspătă*

Concrete code /Mix concrete (weight ratio) *Cod beton/Compoziție (rapoarte masice)*		R	A22	A25	A05
CEM II A-S 42.5 R		1	0.8	0.8	1
IS (dried state)/*IS (uscat)*		0	0.35 substituie 20% ciment şi 20% nisip (0-1 mm)	0.58 substituie 20% ciment şi 50% nisip (0-1 mm)	0.35 substituie 50% nisip (0-1 mm)
Sand/*Nisip*	0-1 mm	0.75	0.60	0.37	0.60
	1-2 mm	1	1	1	1
	2-4 mm	1	1	1	1
Gravel/*Pietriş*	4-8 mm	2.25	2.25	2.25	2.25
Water/cement ratio/*Raport apă/ciment*		0.49	0.60	0.65	0.60
HRWR /*Aditiv puternic reducător de apă* (%)		0.7	0.7	0.7	0.9
Unit weight /*Densitate* aparentă (kg/m^3)		2350	2196	2197	2201
Consistency (by flow table test)/*Consistența (metoda răspândirii)* (cm)		14	12	13	16

Table 2

The physical characteristics of IS waste/*Caracteristicile fizice ale deşeului IS*

Particle size /*Dimensiune particule* (%)			Density/*Densitate* (kg/m^3)	Bulk density /*Densitate în grămadă* (kg/m^3)
< 0.125 mm	< 0.25 mm	< 0.5 mm		
85.4	96.8	99.8	2133	691

Table 3

The chemical composition of IS from landfill / *Compoziția chimică a nămolului IS prelevat de la haldă*

Chemical compound/*Compus chimic*	Content from....to *Conținut de la...până la* (%)
Insoluble in HCl/*Parte insolubilă în HCl*	3 - 8
Organic compounds (and coal)/*Compuşi organici (şi cărbune)*	20 - 40
CaO	15 - 25
MgO	3.0 - 5.0
Fe_2O_3	5.0 - 11.0
Al_2O_3	0.3 - 0.7
Cr_2O_3	0.2 - 0.4
SiO_2	0.2 - 1.5
Sulfur (total)	4.0 - 11.0
NaOH	2.0 - 20.0

The hydraulic reactivity of IS toward calcium hydroxide can be appreciated by the Si and Al solubility both into demineralized water at own pH and into basic leachant (NaOH 0.1N). The pH and L/S ratio influence on the Si and Al leaching from IS waste is showed in Figs. 1 and 2. The greatest Si and Al solubility was into NaOH solution, with pH=12, like the one of the cement matrix pores aqueous solution. The Si and Al leach from IS waste is a favorable premise of its pozzolana character. It is known that the pozzolanic reaction is concretized by calcium silica aluminate hydrates precipitation, of the hardening cement pastes structure.

The pozzolanic character of IS sludge was tested by the compressive strengths evolution of the paste with 25% Portland cement and 75% different powders. The results are given in Table 4. The favorable compressive strength evolution up to 180 days of A2 samples was observed. Also, the higher value of compressive strength of A2 sample for 180 days of 28.3 MPa than the reference (A2N) of 18.6 MPa, suggest some pozzolanic potential of IS.

The leaching properties of the IS waste were also investigated. The leaching test was carried out at pH =7 (own pH of material) and at pH=12. The chemical speciation concentration values are showed in Table 5.

The heavy metal release was influenced by pH [20]. According to experimental leach data, Cd release was favorable influenced by a neutral pH value, but Cu release was accentuated into strong basic leachant, at pH of 12. The SO_4^{2-} anions release was decreased at higher L/S ratios.

3.2. The properties of concretes with IS waste addition

The A25 concrete with the greatest IS waste content, was tested by monolithic leaching test. The monolithic leaching test based on the mass transfer mechanism at solid/liquid (included into pores)/interface [21-23], is suitable for studying the contaminants release from the concrete matrix, as porous solid which included IS waste, to the aqueous media included into pores.

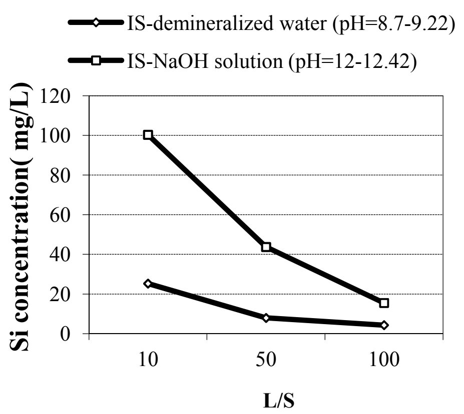

Fig. 1- The pH and L/S ratio influence on the Si compounds solubility of the inorganic sludge/*Influența pH-ului şi a raportului L/S asupra solubilizării compuşilor cu Si din nămolul anorganic.*

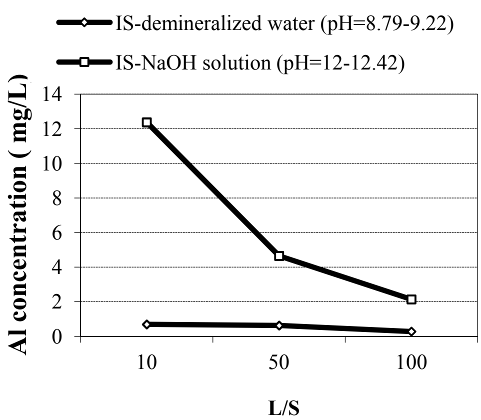

Fig. 2 - The pH and L/S ratio influence on the Al compounds solubility of the inorganic sludge / *Influența pH-ului şi a raportului L/S asupra solubilizării compuşilor cu Al din nămolul anorganic.*

Table 4

Compressive strengths evolution of the pastes with cement and various powders
Evoluția în timp a rezistenței la compresiune pentru pastele cu ciment şi diferite adaosuri pulverulente

Sample code *Cod probă*	Mix (weight %)/*Compoziție* (% de masă)				Compressive strength at : *Rezistența la compresiune (MPa) la:*			
	CEM I/42.5N	Sand particle size /*Nisip* <0.2 mm	Glass powder *Pulbere de sticlă* <0.2 mm	IS waste *Deşeu IS* <0.2 mm	2 days *2 zile*	7 days *7 zile*	28 days *28 zile*	180 days *180 zile*
A2N	25	75			7.2	10.5	18.1	18.6
A2E	25		75		5.5	7.5	12.2	38.5
A2	25			75	6.6	8.6	13.4	28.3

Table 5

The release of chemical speciations from IS waste at own pH and at pH =12 for different L/S ratios according to dynamic extraction leaching test /*Valori ale emisiilor din deşeu la pH propriu şi la pH=12 la diferite valori ale raportului L/S conform testului de extracție dinamică*

Sample code *Cod probă*	*L/S ratio/Raport L/S*	Concentration/*Concentrația* (mg/L)									
		Cd	Ca	Mg	Cu	Ni	Pb	Zn	K	SO_4^{2-}	CO_3^{2-}
IS-A	10	0.07	35	1.82	0.12	<0.05	0.012	<0.05	180	270	160
	30	0.019	37	1.6	<0.001	<0.05	<0.001	<0.05	2	19	270
	100	0.003	37	0.73	0.008	<0.05	<0.001	<0.05	2.3	35	200
IS-AB	10	0.005	48	0.43	0.19	<0.05	<0.001	<0.05	22	190	190
	30	0.015	11	0.5	0.084	<0.05	<0.001	<0.05	7.1	83	230
	100	0.001	5.7	0.22	0.011	<0.05	<0.001	<0.05	3.3	40	250

IS –A: demineralized water as leachant/*s-a folosit ca lixiviant apa demineralizată*; IS –AB: NaOH 0.1 N solution as leachant/*s-a folosit ca lixiviant soluția de NaOH 0.1N*

The eluates obtained were used for analyze of contaminants concentration. Also, just after eluate collection it was measured electrical conductivity and pH. The pH and the electrical conductivity of the leachates were characterized by fluctuant values reasonably likely due to solubilization of basic compounds from the analyzed samples and, on the other hand, dissolution of a atmospheric CO_2 during the storage, sampling and processing of the leachates (Fig. 3).

The measured cumulative release of some chemical species is given in Figs 4 and 5. The similar plot of Ca and sulfate release (Fig. 4) can be attributed to calcium sulfate solubilisation. The relatively low concentration of soluble sulphate ion (from sodium sulfate) can be considered an effect of its partial precipitation as ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) and monosulfate ($3CaO{\cdot}Al_2O_3{\cdot}CaSO_4{\cdot}12H_2O$).

The heavy metals Pb, Cr and Cu increasing release trend diminished during time, after a logarithmic plot. This variation mode of heavy metal concentration is adequate of a diffusion mass transfer.

The leaching behavior of the concretes with IS waste addition is important for making decision on the area of use. The results given in the Table 6, concerning the emission of heavy metals, may be a prerequisite classification of concrete with the addition of IS as a construction material U1, according to Dutch Building Material Decree - DBMD [24].

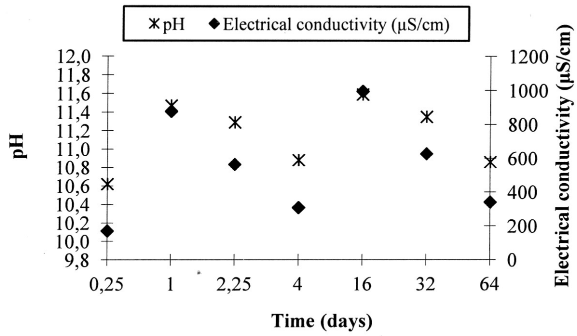

Fig. 3 - The pH and electrical conductivity values of the A25 concrete MLT leachates/*Valori ale pH-ului şi conductivității electrice ale soluțiilor de lixiviere monolitică (MLT) a probei A25.*

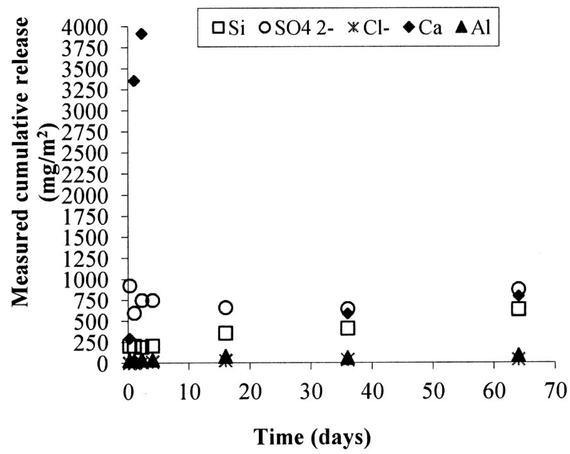

Fig. 4 - The MLT cumulative release of Ca, Si, Al, sulfate and chloride ions from A25 concrete/*Emisiile cumulate ale Ca, Si, Al, ale ionilor sulfat şi clorură în soluțiile de lixiviere monolitică a probei de beton A25.*

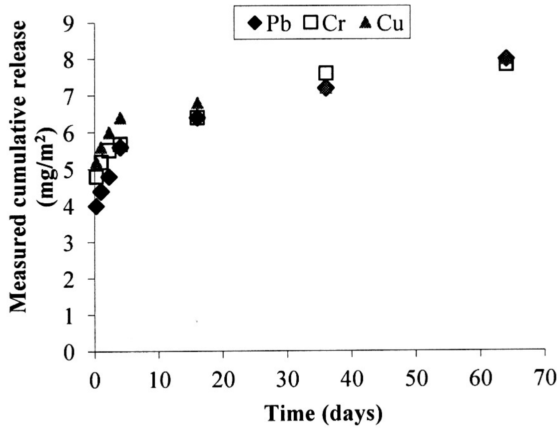

Fig. 5 - The MLT cumulative release of Pb, Cr, Cu from A25 concrete/ *Emisiile cumulate ale Pb, Cr, Cu în soluțiile de lixiviere monolitică a probei de beton A25.*

Based on the MLT data it was possible to calculate the imission (I_c), by equation according to [24]:

$$I_c = E(64d) \times f_{temp} \times f_{ext} \times \sqrt{f_{bev} \times f_{iso}} \quad (3)$$

Where: E (64d) is laboratory result for emission, mg/m^2;

f_{temp} - correction factor for temperature lab-practice (0.7);

f_{ext}- extrapolation factor from 64 days to 1 and 100 years (2.4 for sulfate and chloride for 1 years; 15 for all other components for 100 years);

f_{bev} – correction for limited moistening period (0.1-limited moistening);

f_{iso} – correction for a work with isolation measures (1 - no isolation).

Table 7 gives the calculated imission values obtained for main constituents of matrix concrete with IS waste addition and the required values according to [24].

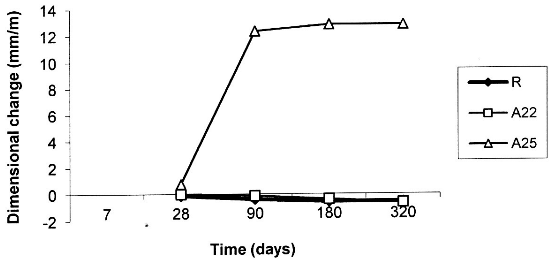

Fig. 6 - The dimensional changes of concretes/*Variațiile dimensionale ale betoanelor testate*

The increasing of IS waste content contribute to expansion of concrete prismatic samples. So, the 320 days age A25 concrete expansion value was about 12.87 mm/m. The A22 concrete sample, with a lower content of IS waste, showed a low shrinkage of 0.625 mm/m, comparable to reference concrete, R, of 0.55 mm/m (see Fig. 6).

The water absorption had an increasing trend (up to 5%), after 100 days of concrete sample immersion (fig. 7). The A25 concrete sample water absorption show a good correlation with expansion very probably due to the ettringite precipitation over time.

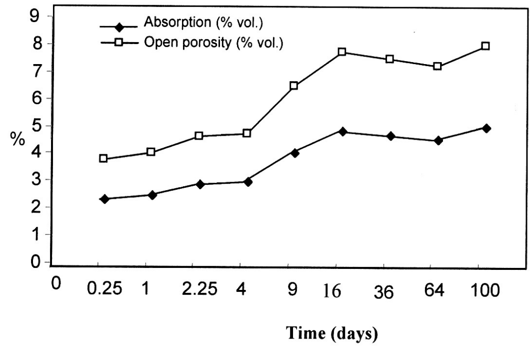

Fig. 7 - The A25 concrete water absorption evolution over time/*Variația în timp a absorbției de apă a betonului A25.*

Table 6

The measured cumulative emission values of the contaminants from A25 concrete (after 64 days) according to MLT
Emisiile cumulate ale contaminaților din betonul A25 (după 64 zile), în conformitate cu testul de lixiviere monolitică

Code of concrete with IS waste *Cod beton cu deşeu IS*	Contaminant *Contaminant*	Cumulative emission/*Emisie cumulată* (mg/m^2)	DBMD demand emission *Emisii conform DBMD* (mg/m^2)	
			U_1	U_2
A25	Pb	40	100	800
	Cr	43	150	950
	Cu	45	50	350
	SO_4^{2-}	5224	25000	200000
	Cl^-	135	20000	150000

Table 7

The chemical speciation cumulative imission values of the concrete with IS waste according to MLT
Imisiile cumulate pentru speciile chimice din betonul cu deşeu IS, în conformitate cu testul de lixiviere monolitică

Imission/*Imisii* (mg/m^2)	Na	Pb	Cr	Ca	Cu	Cl^-	Si	Al	SO_4^{2-}
1 year/ *1 an*	-	-	-	-	-	21	-	-	468
100 years/*100 ani*	3188	27	26	2656	27	-	2125	292	-
Required values according to DBMD/*Valori conform cerințelor DBMD*	-	1275	-	-	540	-	-	-	45000

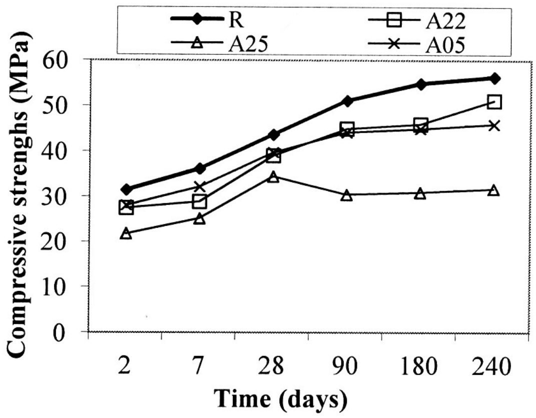

Fig. 8 - The concrete compressive strengths evolution
Evoluția în timp a rezistenței la compresiune.

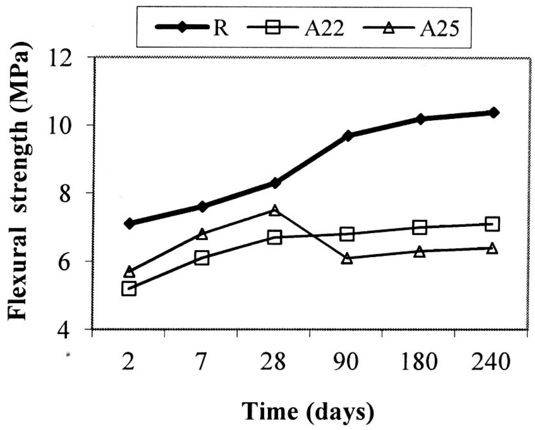

Fig. 9 - The concrete flexural strengths evolution/*Evoluția în timp a rezistenței la încovoiere.*

The mechanical strength of concrete is commonly considered its most valuable property. It is generally known that the development of mechanical strength is due to the growth of interlocking crystals and cohesion developed by gelic calcium hydrosilicate during the hydration process of binder. It is also knows that the concrete strength development is controlled by the cement matrix, the aggregates and the interfacial bond between the cement matrix and the aggregates.

The results of concrete strengths testing clearly showed that as the increase of waste amount in the concrete leads to decrease of the mechanical strengths. In Fig. 8 it can be seen that compressive strengths of A22 and A05 concrete samples have continuously increasing trend up to 240 days concrete age (up to 51.2 MPa and respectively, 46 Mpa). The flexural strength of the various concretes showed similar results as the compressive strength. The flexural strengths decrease comparative to the reference is more significant than de compressive strength (Fig. 9). There is a decrease of the flexural strength after 28 days concrete age (Fig. 9).

The decrease of compressive and flexural strengths of A25 samples after 28 days can be a consequence of the IS waste highest content and therefore of major content of sulfate ions from waste.

Sodium sulfate provided by waste reacts with calcium hydroxide to produce secondary gypsum, according to the reaction (1) [25]:

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH \quad (1)$$

Gypsum have a lower solubility (0.01 mole/l at 25°C) than calcium hydroxide (0.02 mole/l at 25°C) and precipitates out, while $Ca(OH)_2$ dissolves to replenish Ca^{2+} [26-28]. The gypsum can react with aluminum bearing phases to form ettringite following to the reaction (2):

$$4CaO \cdot Al_2O_3 \cdot 13H_2O + 3(CaSO_4 \cdot 2H_2O) + 14H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + Ca(OH)_2 \quad (2)$$

The dangerous ettringite expansion processes in A25 concrete is developing whether it
nant potential of the concrete with IS addition for water and soil; such as the heavy metal, cumulative

Has precipitated after concrete hardening.

Calcium hydroxide continues to react with sodium sulfate with gypsum formation; this one participates to reactions whose product is etringitte. So, the forming of the etringitte through reactions between the alkali sulfate from the IS and the components of the cement matrix should be one of the major causes of the sulfatic expansion which have as consequences internal tensions and cracking of the concrete. On the hand other is known the ettringite potential of immobilising Cr^{3+} and CrO_4^{2-} ions [29].

4. Conclusions

The influence of inorganic sludge, IS, from paper industry, on the concrete properties has been investigated.

- The IS waste was characterized as a pozzolana addition according to the standard pozzolanic activity index and due to the solubility of Si and Al from IS waste into NaOH 0.1N leachant that simulates the solution of concrete pores. Also, the IS waste pozzolanic potential was revealed by the 180 days-compressive strength value of the cement - IS waste hardened paste (of 28.3 MPa), higher than of the cement - fine sand reference mix (of 18.6 MPa). The leaching properties of the IS waste were tested by extraction leaching test at own pH and basic pH of 12 to simulate the aqueous media of cement matrix pores with IS waste addition.

- The A25 concrete, with the greatest IS waste addition, as substitute, of 20% cement and 50% fine sand, was selected for monolithic leaching test in order to evaluate the concrete matrix ability to heavy metals immobilize. The heavy metals Pb, Cr, Cu increasing release trend was diminished during time, after a logarithmic plot. This variation mode of heavy metal concentration over time is appropriate of a diffusion mass transfer. The heavy metals release, according to monolithic leaching test, suggested a low contaminant potential of the concrete with IS addition for water and soil; such as the heavy metal, cumulative release, in mg/m^2, was of 45 for Cu, of 43 for Cr and of 40 for Pb.

The relative low concentration of soluble sulfate ion in eluates can be the effect of its partial precipitation as etringitte, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$, the main factor of expansion and cracking of concrete with the greatest IS waste content.

- The A22 concrete, with 20% IS addition as cement substitute and 20% IS addition as fine sand substitute showed a shrinkage evolution closed to the reference concrete and a continuous mechanical strengths increasing evolution.

-The inorganic sludge, although it showed a hydraulic activity, can substitute the cement in concrete in relatively low proportion, less than 20% according to obtained data, referring to 240 days-compressive and flexural strengths (compressive strength of A22 concrete was 51.2 MPa, of reference concrete was 56.4 MPa, while the flexural strength was 7.1 MPa and, respectively, 10.4 MPa).

-Consequentlly, the recovering of IS waste from paper and pulp industry by washing to remove sodium sulfate, would be beneficial for the use as secondary raw material with pozzolanic properties for concrete.

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