SOLUZIONI AMBIENTALI
ENVIRONMENTAL SOLUTIONS

Co-funded by the Eco-innovation
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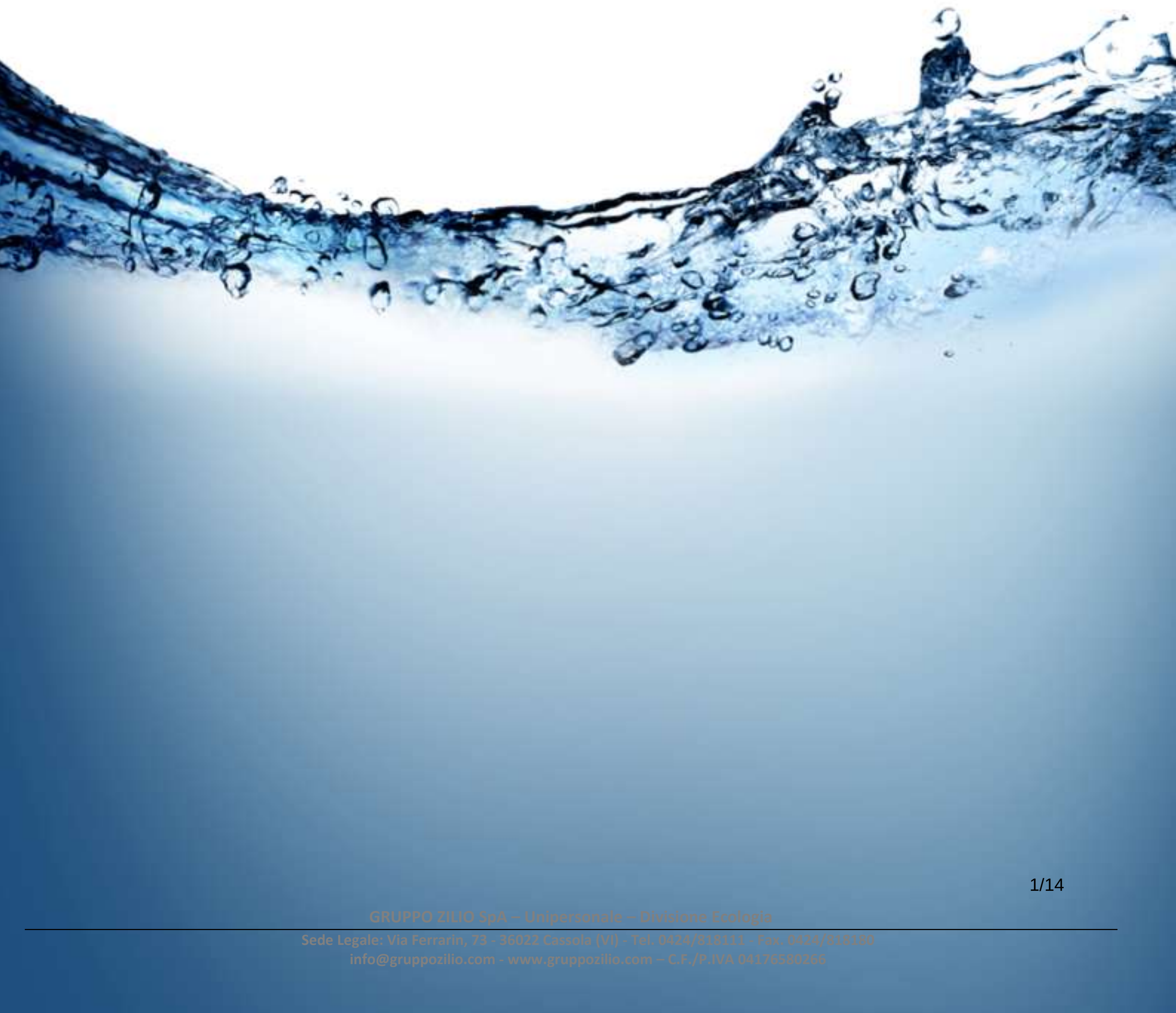
regenera

Regenerable high efficiency filtering media
for arsenic treatment in drinking water



GRUPPO ZILIO SpA – Unipersonale – Divisione Ecologia
Sede Legale: Via Ferrarin, 73 - 36022 Cassola (VI) - Tel. 0424/818111 - Fax. 0424/818180
info@gruppozilio.com - www.gruppozilio.com – C.F./P.IVA 04176580266

Indice:

GRUPPO ZILIO SpA – Unipersonale – Divisione Ecologia
Sede Legale: Via Ferrarin, 73 - 36022 Cassola (VI) - Tel. 0424/818111 - Fax. 0424/818180
info@gruppozilio.com - www.gruppozilio.com – C.F./P.IVA 04176580266

1. IRON OXIDE-HYDROXIDE FOR THE REMOVAL OF ARSENIC REGENERATION PLANT

The plant for the regeneration of iron oxide-hydroxide saturated with arsenic started operation in October 2013. Together with a plant for the production of an iron oxide-hydroxide filtering material, this plant was co-financed by the European Union within the framework of CIP Eco-Innovation Programme. This project has been chosen as one of the five success stories to be presented at 18th Eco- Innovation Day (Barcelona, 20-21 May 2015), the yearly event of the European Union dedicated to innovation for environment.

The principle of operation is a straightforward derivation of a property of iron oxide-hydroxide, that adsorbs very well arsenic at low pH, but releases it at high pH. The plant operates with an intimate contact between the material and a suitable caustic solution for the time required to desorb arsenic. After desorption, the material is rinsed with an acidic solution until the pH reaches a value compatible with reuse of the oxide-hydroxide in contact with potable water for human consumption. The plant has three main parts: the first for the true regeneration, the second for the precipitation of arsenic from the regeneration fluid that contains the arsenic removed from the material, and the third for the dewatering of the sludge obtained in the preceding step.

1.1 Regeneration Section

Two equivalent reactors, capable of parallel operation, are the essential part of the regeneration section. The material to be treated is loaded into the reactors and contacted with a flow of sodium hydroxide. After desorption of arsenic, the regeneration fluid enriched in arsenic is sent to the second section of the plant. The material in the reactors is regenerated now, but its pH is very high and must be neutralized. This is done with a flow of water that is constantly acidified while entering into the reactor, its pH is monitored when it exits the reactor, and the process is continued until the solution leaving the reactor is neutral. At the end of the process the material can be unloaded and is ready for reuse.

Regeneration Section

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1.2 Arsenate Precipitation Section

The second section of the plant has a set of tanks for the chemicals needed to precipitate the arsenate efficiently and a stirred vessel where the precipitation takes place. The first operation is adjusting the pH to the optimum value for quantitative precipitation, then ferric chloride is added to co-precipitate the arsenate. Now the pH is adjusted to the optimum value for flocculation and a flocculant is added. The sludge is then allowed to sediment at the bottom of the vessel. After sedimentation, the sludge is sent to the next section of the plant, while the surnatant, that is clear water with no arsenic now, is sent back to the beginning of the process and reused for a new cycle of caustic treatment.

Precipitation Section

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1.3 Dewatering Section

The last part of the plant is the dewatering of the sludge, that is done with a filter press. The water coming out from the filter press has the same composition of the surnatant of the preceding step, and is sent at the beginning of the process as well. The arsenic contained originally in the spent material is in the filter cake now, and this is the only waste that must be landfilled.

Dewatering Section

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1.4 Conclusion

The plant has been in operation for about one and half year, as of now (May 2015). We have a few significant data about performance and capacity of the plant in a regime condition. The plant needs a special authorization from local authorities to be operated, because it treats a waste, and each year we must prepare a summary of what we have done in the previous twelve months. At the end of April 2015 we have sent the first summary, that covered a longer period because it included also a few months of commissioning and adjustment of the operating parameters. So we have fresh data available. During the period covered by the report, we have received 172 tons of saturated iron oxide-hydroxide from many different plants in Italy. We have regenerated 124 tons of material, and 84 of these have been reused. All the material reused is working as expected in 11 filters scattered in 6 different water treatment plants. We are constantly monitoring the performance of the material in all the plants. For example, the first 16 tons regenerated were reinstalled in a plant in Velletri (middle Italy), in two different filters, at the beginning of February 2014. In this site, the concentration of arsenic in raw water is very high, usually above 50 µg/l, and there is also a fairly high content of vanadium (slightly variable, but usually more than 40 µg/l). The table here below summarizes the concentration of arsenic in the treated water from May 2014 to April 2015.

Filter code	Filtration start date	Sampling date							
		7-5-2014	5-6-2015	18-7-2014	6-8-2014	4-9-2014	1-10-2014	4-11-2014	20-4-2015
C1-VA1	10/02/2014	3	2	4	4	3	4	3	6
C2-VB1	10/02/2014	3	3	5	<2	0	2	<2	7
Raw water	N.A.	51	57	53	53	49	57	54	49

As can be clearly seen from the table, after 14 months of operation the concentration of arsenic in the treated water is still well below the limit of 10 µg/l.

A few further general comments.

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This plant is a true "zero liquid discharge". No liquid waste is produced and the same water is continually reused. The only water "consumption" is the very limited amount that wets the regenerated material and the filter cakes (but this is unavoidable and negligible). The positive impact of the plant on the environment is dramatic, and most probably one of the reasons why this project was co-financed by the European Union and considered to be one of the success stories. Without this plant, all the arsenic saturated material from water treatment plants should be landfilled. On the other hand, thanks to this plant, the waste to be landfilled is only approximately 3% of the total mass regenerated. This plant is the first in Italy to treat a waste of this kind to obtain a secondary raw material. Last but not least, this is the first plant of this kind built in the world and as far as we know, still the only one.

An interesting article about iron oxide-hydroxide regeneration (*Abraham S.C. Chen, Thomas J. Sorg, Lili Wang, 2015. Regeneration of iron-based adsorptive media used for removing arsenic from groundwater. Water Res. 77 (2015) 85-97)* appeared recently in specialized literature. It gives an outlook on the state of the art in this field, and clearly shows that work on this subject is in the very early stages, still at the laboratory level, in the United States: the stage at which Gruppo Zilio was five years ago.

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2. IRON OXIDE-HYDROXIDE FOR THE REMOVAL OF ARSENIC

GRUPPO ZILIO NEW PLANT

The plant for the production of iron oxide-hydroxide started operation in Cassola during April 2015. Together with a plant for the regeneration of iron oxide-hydroxide saturated with arsenic, this plant was co-financed by the European Union within the framework of CIP Eco-Innovation Programme. This project has been chosen as one of the five success stories to be presented at 18th Eco- Innovation Day (Barcelona, 20-21 May 2015), the yearly event of the European Union dedicated to innovation for the environment.

General View of the Plant

The plant has several sections, that will be described in this report together with their most significant features.

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2.1 Reaction Section

The first section has for reactors, operating in parallel, where the chemical reactions at the root of the process take place. The chemistry in this section is not new, but the reactors, dosing pumps, control instrumentation for weights and other relevant reaction parameters, have been selected among the newest and most reliable available on the market.

Reaction Section

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2.2 Cross- flow Wash Sections

The second section has the purpose of washing the iron hydroxide in a cross-flow apparatus. During the reaction step, together with the iron hydroxide, also a stoichiometric amount of sodium chloride is produced. Sodium chloride is an unwanted by-product, and must be removed from the reaction mixture with a thorough washing. This is a well known operation, but we do it in a very innovative ultra-filtration apparatus.

In the Cassola plant we use silicon carbide ceramic membranes, that are permeable to salty water, but impermeable to iron hydroxide. In this way, clear water is continuously substituted for salty water permeated through the membranes, until the salt concentration is lowered to required level. The relevant feature for this application of the silicon carbide membranes, is their extremely high permeability, that allows treatment of fluids with very high solids concentration. So in this part of the plant the reaction mixture can be pre-concentrated, before salt removal. And hence a reduced volume of fluid is left for washing, instead of all. The consequence is a great saving of raw water, with an obvious positive impact on the environment. In addition, after washing the iron hydroxide is much more concentrated than with a traditional cross-flow washing, and this has a very high impact also on the quality of the finished product.

Cross-flow Wash Section

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2.3 Filter Press Section

In the third section, the material washed in the preceding section if dewatered with a filter press. In this case too, the technique is well known, but in the Cassola plant we use a filter press especially made for this purpose. This filter press is of the membrane type, where the cake is further dewatered "inflating" the membranes at high pressure after the first traditional pressing. The "squeezing" of the cake leads to a final cake with a solids content impossible to obtain with traditional equipment, and this is of the utmost importance in view of the further steps of the process and the final quality of the product. The water coming out of the press is much more than with a traditional press, and since this water is completely recycled to react a new batch of material, there is also a further saving of water.

Filter Press Section

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2.4 Freeze-thawing Section

The last section is the freeze-thawing. What is meant by freeze-thawing, in this context, is the granulation of a sludge by means of freezing and thawing. This is the crucial step of the process, and the last operation that decides the quality of the product. An application for a European patent has been filed to protect this step (and hence all the process, being this the last step that implies all the preceding steps). The freeze-thawing in the Cassola plant is simple and effective, and leads to a final product with the same chemical composition, the same appearance, the same compliance with the applicable norms as that produced by other plants, BUT that is morphologically different and proved to be superior in adsorption tests.

Freeze-thawing Section

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3. MAIN FEATURES OF THE IRON OXIDE-HYDROXIDE PRODUCED BY THE NEW GRUPPO ZILIO PLANT

The material produced by the new Gruppo Zilio plant in Cassola belongs to the group of the arsenic adsorbers based on iron oxide-hydroxide. It is produced by reaction of ferric chloride with sodium hydroxide, as a colloidal suspension.

After concentration, washing, and filter pressing, the colloid is converted to a mechanically stable granulate. Granulation is done by freeze-thawing, according to a process currently being patented, and in turn it is made possible by the way in which the preceding steps are done. The resulting material is similar to those usually found on the market as far as composition and granulometry are concerned, and complies with DIN EN 15029. But some features have been improved, owing to this new process, and namely adsorption capacity, specific surface and regenerability. Adsorption capacity of arsenic, in particular, is much higher than competing materials. The reason for this is the very high specific surface as compared to that of competing products.

The following table summarizes the results of one out of many batch tests of adsorption that have been done. In the test, a weighed amount of material is contacted with a solution of known arsenic concentration for a certain time, until equilibrium is reached. The material adsorbs arsenic, and from the final concentration in the solution it is possible to determine the exact amount adsorbed.

Manufacurer	Specific surface BET (mq/g)	Wet mass	Dry mass	% solids	Adsorbed arsenica at saturation (mg)	Adsorption capacity (wet) (mg As/g)	Adsorption capacity (dry) (mg As/g)
Gruppo Zilio	349	0,51	0,25	49,02	14,4	28,24	57,60
Competitor	303	0,51	0,29	56,86	13,6	26,67	46,90

The table compares Gruppo Zilio new product with a competitor. There is clearly a superior adsorption capacity of the new product, that is higher even if the solids content is lower. Considering the adsorption capacity with respect to solids content, the difference is still greater (adsorption capacity higher by as much as 20%), and shows very well how effective the granulation step in our production process is. In our process, the granulation step fully exploits the properties of the material, exactly because it leads to a very high specific surface, as shown in the first column of the table. Last but not least, this leads also to a material that is nearly completely regenerable, whereas other products on the market are regenerable, but to a lesser extent, in the range of 70-80 %.

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