Water treatment in Cinkarna Celje

A water treatment project that includes existing pumping plant at Hudinja river as well as a new water treatment facility, is being carried out in Cinkarna Celje.

Why a new water treatment facility? With this project Cinkarna intends to increase production of TiO_2 and to increase its market share. Acquisition of new water treatment facility will improve water quality, meaning cleaner final product and more reliable production, fully automated and centrally controlled.

Project approach

The first step of a systematic project approach implemented in cooperation with experts from Cinkarna Celje was a design of an outline scheme for a technological facility.

In the next step measurements on the barrage and pilot tests were performed in order to obtain accurate water data. The measurements mentioned above had been performed in cooperation with experts from Jožef Štefan Institute, with whom we carried out technological project of water treatment further on.

Results of measurements and pilot tests represented a starting point for the beginning of work.

A description of the technological process and its main characteristics is given in continuation.

Chemical / technological part of clarification.

Input data represented entry for design and calculation of technological complex.

Type of water Conductivity	Avg. flow	Max. flow	Susp. matter	
Conductivity	(m ³ /h)	(m³/h)	(mg/L)	(µS/cm)
Decanted	474	644	30	
Filtered	451	585	0	435
De-carbonized	176	210	0	100
De-mineralized	134	168	0	5

Based on available analytical data of Cinkarna Celje as well as on our own analyses performed on raw water from Hudinja river, we have defined the following composition as the initial quality of a clear water:

Total hardness	15 °N max.
HCO ₃ ⁻	12,6 °N max.
HCO ₃ ⁻	11,0 °N min.
SiO ₂	4 mg/L
KPK	$30 \text{ mg O}_2/\text{L max}.$

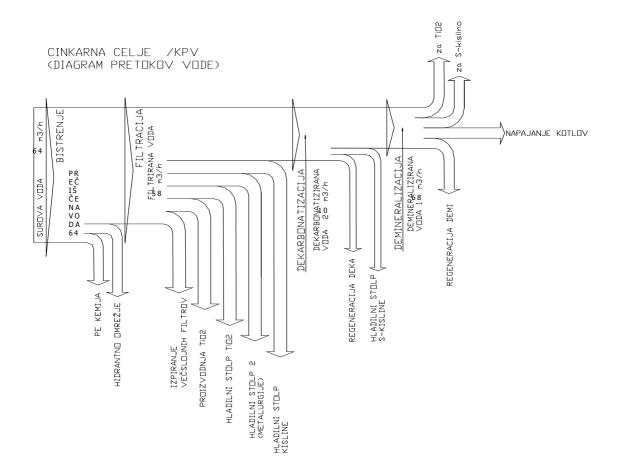
Са	3,0 eq/m ³	
Mg	2,6 eq/m ³	
Na+K	0,2 eq/m ³	
Total K	5,8 eq/m ³	
HCO ₃	4,5 eq/m ³	
NO ₃ + Cl	0,4 eq/m ³	
SO ₄	0,85 eq/m ³	
SiO ₂	0,07 eq/m ³	
Total A	5,8 eq/m ³	
Т	approx.	15 ° C
рН	approx.	7,5

The assumption was adopted that a raw water contained from 0 to 100 g, and for a short time maximum 500 g of suspended matter / m^3 . During possible extreme loadings with suspended particles in time of heavy raining, this value could be higher, but river silt deposits better than mud, composed of coagulant's floccules.

A review of estimated operational parameters of input water and output dregs is given below:

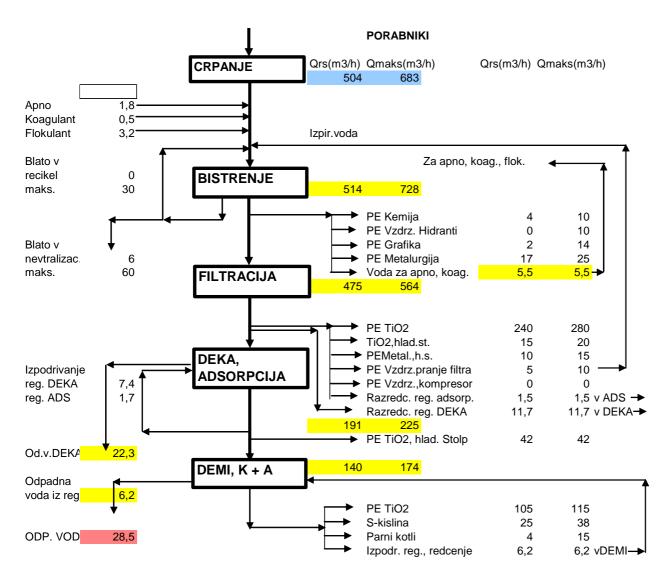
	Dry season	Slight precipitation	Maximum	
Extreme Turbid in the water (mg s.s./L): Solid in dregs (kg s.s./m ³):	50 12,5	150 15	4000 55	9000 94
Mean dregs flow in neutralization of TiO ₂ (m ³ /h):	5,6	9,8	32	64

CONSUMERS INSIDE CINKARNA



OVERVIEW OF THE SYSTEM

Water balance



POVZETE	K REZULT	ΑΤΟΥ	(MAKS PRETOKI)								
			BISTR.	FILTRAC	DEKA	DECO2	ADSORPC	DEMI K+A		CRPANJE	
Qnommak	(m3/h)		728	564	225	225	225	174	Qnommak	683	(m3/h)
Qdnevna	(m3/dan)		17472	13524	5407	5407	5407	4181	Qdnev.mal	16380	(m3/dan)
Qdejanska	(m3/h)	skupaj	728	567	232	225	232	180	Qdnev.sree	12084	(m3/dan)
	Dnevni	cas reg(')	0	10	45	0	45	45	Qletna sree	4410660	(m3/a)
Qdejanska	(m3/h)	1 PROGA	364	142	116	113	116	90			
Stev. Prog	v obrat.		2	4	2	2	2	2			

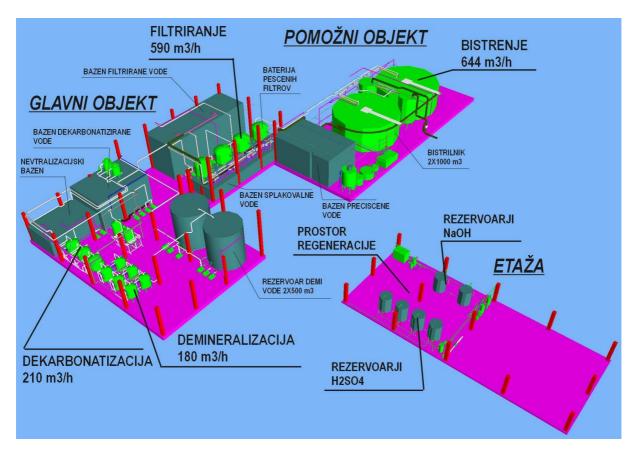


Fig. 1: View of the total water treatment facility

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2. Part 2 CLARIFICATION

The first step in preparation and treatment of water after its pumping from Hudinja river and transport to Cinkarna locality is clarification.

The first stage in raw turbid water preparation is setting the optimal pH value by addition of lime milk, followed by coagulation with addition of an inorganic coagulant, for example a solution of aluminum sulphate. The first stage is carried on in a separated mixing reactor, which provides sufficient dwell time for optimal formation of floccules. Floccules of aluminum hydroxides bind suspended matter. For better separation of formed floccules, organic polyelectrolytes - flocculants - that bind floccules, speed up depositing and increase clarity of obtained water, are added. Flocculation is performed when floccules of an inorganic coagulant are formed, that is in the second mixing reactor, serially connected to the reactor for pH regulation and coagulation. Separated flocculation, activated only when coagulation is already accomplished to a significant degree, increases the efficiency of floccules formation, efficiency of elimination of suspended matter and efficiency of consumption of expensive reagents. This solution is therefore more efficient than coagulation and flocculation performed simultaneously, in the same reactor vessel. This later solution

has been offered by certain suppliers in the form of combined "reactor" and depositor. Apparently simpler solution (everything takes place in a depositor vessel) doesn't offer any practical advantage in terms of equipment design; however, it suffers from less efficient simultaneous coagulation and flocculation of not yet completely formed floccules of the coagulant.

Optimally coagulated and flocculated water spills over into the depositor, where it pours through the inlet shaft into a lower part and enters active mud dregs. Dregs level is permanently measured and maintained at a certain level by removing mud at the bottom and returning dregs from the bottom into the inlet shaft if necessary. Permanent, controlled volume of dregs assures constant quality of filtration of freshly coagulated dregs through a layer of active dregs at the bottom of the depositor. In this process fine particles in interaction with bigger floccules are combining, thus increasing the efficiency of clarification.

Besides separating solid particles combined in floccules from clear water, the two depositors have a task of containing dregs in case of failure of fittings or equipment after the depositor. 1 m^3 of dregs can contain approx. 54 kg of suspended matter, therefore a spare volume of dregs at 1 m depositor's height is sufficient for 1 to 4 days (24 h/d) of operation without draining dregs at the medium or heavy loading of water with suspended particles.

In dimensioning equipment for water clarification we have started with our own, as well as with those recommended by reagent suppliers, empirical values for particular parameters, such as the speed of floccules sedimentation, dwell times at floccules formation and the like, but we have also experimentally verified basic parameters in a continuous device with a rate of flow of 250 L/h, which used water from a pumping station at Hudinja river and which have had separated stages of coagulation, flocculation and sedimentation. Values for consumption of chemicals ad additives as well as for measured quality of water (turbidity and conductivity) obtained on trials have been used for dimensioning. By experimental verification of parameters we have been able to achieve greater degree of reliability in dimensioning and design of water clarification operation, while projecting of further operations, such as filtration, removal of organic matter, de-carbonization and demineralization was related mostly to the correct analysis of input water and to empirical parameters, related to the properties of ion exchanging resins.

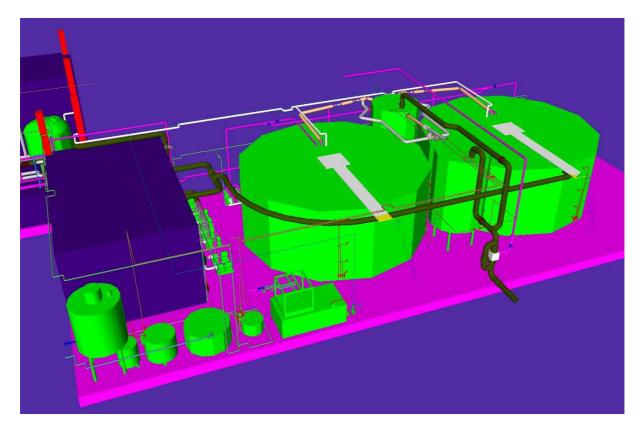


Fig. 2: System of clarification

FILTRATION

Water from the reservoir of clarified water is pumped through four multi-layer filters. In the direction of flow the filters are filled with a layer of hydroanthracite, and filtering and supporting layer of a flint sand. Multi-layer filters operate completely automatically and are intended for separation of impurities (particles, solid particles) by means of a flint sand, what represents filtration of clarified and already partly decarbonized water. A hydroanthracite layer improves filtration capability by considerably increasing filter's filtration volume. Filtration layer of sand operates as the main filtration layer while supporting layer protects filtration nozzles at the bottom of the filter vessel.

Control of the device is performed by measuring pressure drop on the device during operation. If the resistance through filters increases to the preset value, automatic washing of multi-layer filters starts, beginning with the first filter. Filter no. 1 is washed out. After finishing counterflow washing of filter no. 1 washing of the next filter starts.

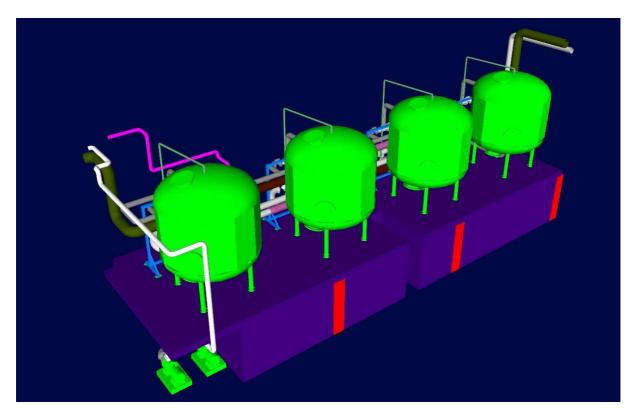


Fig 2: Drawing of the filtration system

Part 3 DE-CARBONIZATION

At this stage calcium and magnesium ions, bonded to hydrogen carbonate ion, are separated from the water.

Filter regeneration is a co-flowing one. Why a co-flowing regeneration? Because in case of a counterflow regeneration there is no control of the proper regeneration. Furthermore, in the normal process it is the upper third of the total mass, which is the most heavily loaded and the back one is less heavily loaded. In the case of counterflow regeneration, a phenomenon of "over-regeneration" of the lower mass layer can occur, as well as the accumulation of lime cake, created during regeneration with H_2SO_4 .

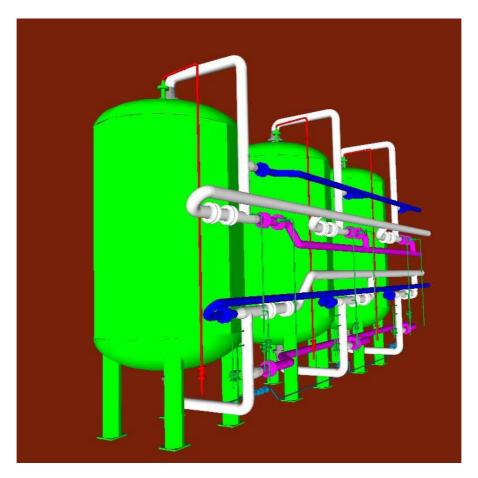


Fig. 3: Drawing of deka system

DEGASING

Calcium and magnesium ions, bonded to hydrogen carbonate ion, are replaced with hydrogen ions and free carbon acid generated during the process is separated by air ventilation in the column with filler. For degassing, two degassers with fan, capacity of 6000 m³/h, are built in. Due to the large volume of air needed, the air intake is from the environment; otherwise a big under pressure would appear in the system.

DEMINERALIZATION

Demineralization consists of a strongly acid and strongly basic exchanger.

At this stage primarily remaining calcium and magnesium ions, bonded to other ions but hydrogen carbonate ones, are separated as well as sodium and potassium cations.

In the second stage, sulphate, nitrate, chloride and silicate anions are removed from the water.

The system operates as a counterflow one, meaning that mass regeneration is performed in the flow opposite to the process of demineralization.

With this system better results can be achieved, with smaller quantities of waste water that have to be neutralized later.

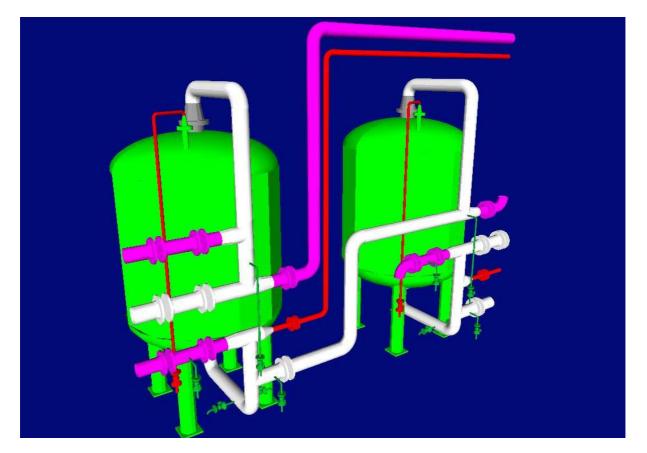


Fig. 4: Drawing of DEMI column

NEUTRALIZATION

In the process of neutralization waste water is collected during the whole process. The water is properly neutralized in a reservoir (pH 6,5 - 8,5). Neutralization is carried out by means of an acid (H₂SO₄) and a base (NaOH). For the purpose of

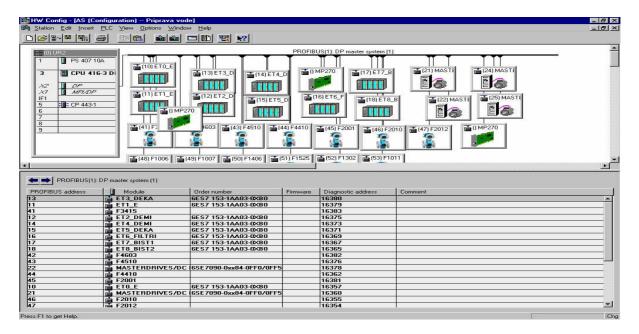
regulation, a complete automatic monitoring is performed, as well as taking samples for further laboratory analysis. Time controlled mixing in a reservoir is performed by means of fluidic nozzle mixers, installed on the bottom of the reservoir. Dosage of H_2SO_4 and NaOH is from measuring reservoirs by means of dosage pumps. The degree of dosage depends on deviation from the reference point for pH value Actual pH value is constantly measured by a pH probe. After certain programmed time of mixing with dosed chemicals (=neutralization) and if required pH value is stabilized in a certain programmed time, the contents of the reservoir are released under control into the outlet.

Part 4 CONTROL SYSTEM

Before designing software for the project, it was necessary – in cooperation with technology experts - to work out a functional specification for the software part. Based on this specification, we have produced control algorithms for the complete technological process.

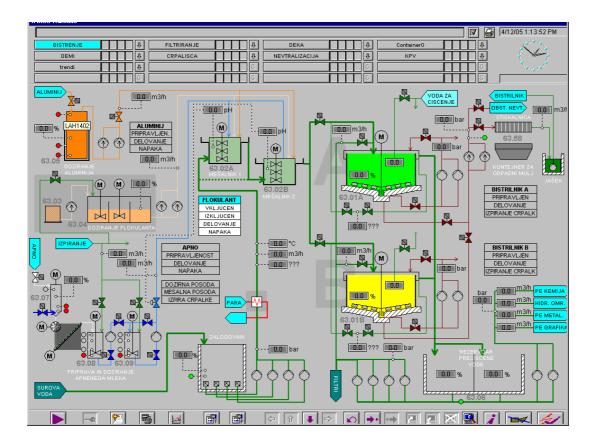
The backbone of the system is Siemens DCS system PCS7. This system is based on hardware components from Simatic family of freely programmable controllers.

Besides input/output peripheral units, frequency converters of motor pump drives and intelligent measurement and regulation equipment as well as MP270 operator's panels for local control and indication of particular functional groups have also been connected to AS416-3 process station.



Nodes on Profibus network operate as equal members. For access to the network a token system is implemented. When the node retains the token, it can start transmitting a message to a certain target. The messages can be addressed to all nodes in the network.

Level of control is implemented in operator's control station, designed as an OSserver and connected to the existing industrial ethernet network via optical link.



Application software

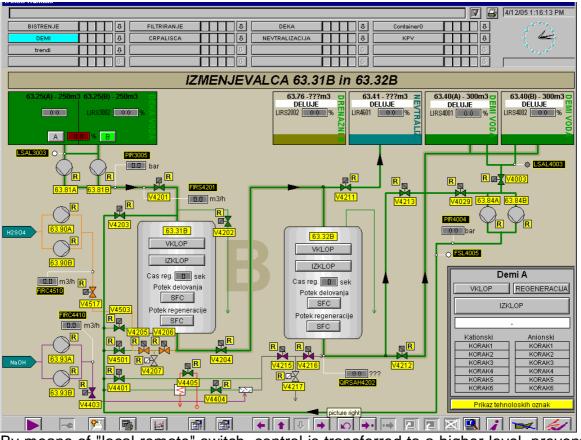
Configuration of hardware and programming of the system have been implemented with programming tools within the framework of PCS7; standard program and functional blocks have been used as much as possible, because of better transparency and maintainability of the system.

WinCC scada collects system data in real time, displays them in an evident manner, archives them and triggers alarms.

It enables system operator visualizing the system, entering regulation parameters, manual switch-on and intervention into the system, alarming, messages to the operator, archiving and the display of the history.

Control system operates in the role of a server and sends data to clients, connected to the industrial ethernet network so, that the operation of the system can be monitored from any computer in the network.

In design of levels of control the basic principle has been hierarchical organization on a particular level.



By means of "local-remote" switch, control is transferred to a higher level, preventing at the same time control from two levels.

The following possibilities of serving exist:

- manual interventions, switching on/off (opening/closing) of a particular

device

- switching on/off, automatic operation of technology groups
- setting desired values for regulation loops

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Data on implemented application

900 kB of program and data code	9
Standard blocks used:	14 organization blocks
	58 functional blocks
	512 functions
	816 data blocks
I/O points used:	912 digital signals
	96 analog measurements
	43 profibus nodes
Scada:	26 main figures and sub-figures
	8350 points

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